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ON THE APPLICATION OF THE ELECTRICAL ANALOGY METHOD TO PRESSURE DISTRIBUTION UNDER WEIRS WITH CAVITIES

By D. C. Midha and V. I. Vaidhianathan

(Irrigation Research Institute, Punjab, Lahore)

Received July 16, 1942

An exhaustive study of the distribution of uplift pressure under weirs constructed on permeable foundations had been carried out by the electrical method at this Institute.* The results of these investigations were applicable to the cases of weirs where there were no cavities in the foundation. If, however, a cavity occurred in the subsoil under the weir, there would be a redistribution of pressure. The object of the present investigation is to find out if the electrical method can also be applied to the study of pressure distribution under a weir with cavities. This required experiments both in hydraulic and electrical models. These experiments have been done with a simple flush floor.

The Hydraulic Model.—Experiments in a sand model were carried out in an iron tank 50 inches long, 8 inches broad and 30 inches deep with a glass front. Sand was packed under water to a height of 22 inches in the tank. A glass plate 12 inches long, 8 inches broad and 1 inch thick was placed on sand with sound contact between the glass and sand. This glass plate corresponded to the impervious floor and was provided with twelve suitably spaced glass tubes passing right through its thickness for measuring pressure at various points just under the floor. Water-tight partitions were built at both ends of the floor for maintaining desired levels of water on the upstream and downstream sides. The lower boundary was kept elliptical in shape to correspond to the infinite depth of the pervious stratum as derived from theoretical considerations.

For the sake of practical convenience the experiments have been carried out with a cavity semi-cylindrical in shape 8″ long and 2″ in diameter. The cavity was scooped out in the sand foundation each time in the desired position and its form was maintained in the course of the experiment by fitting a perforated brass sheet into it. A diagrammatic sketch of the tank with the cavity in the centre of the floor is shown in Fig. 1.

* Gurdas Ram and V. I. Vaidhianathan, *Proc. Ind. Acad. Sci.*, 1940, **12 A**, 245 and earlier papers.

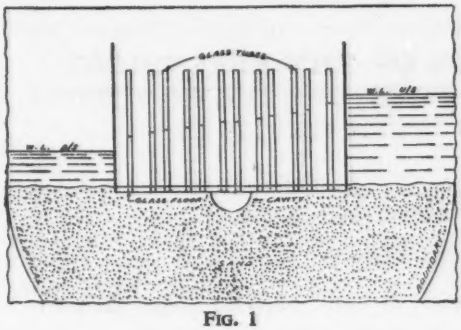


FIG. 1

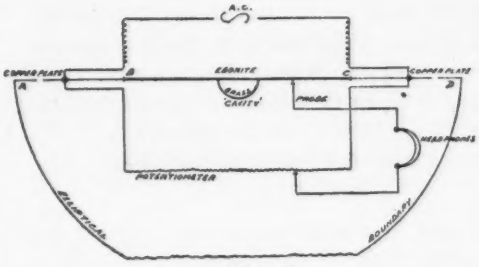


FIG. 2

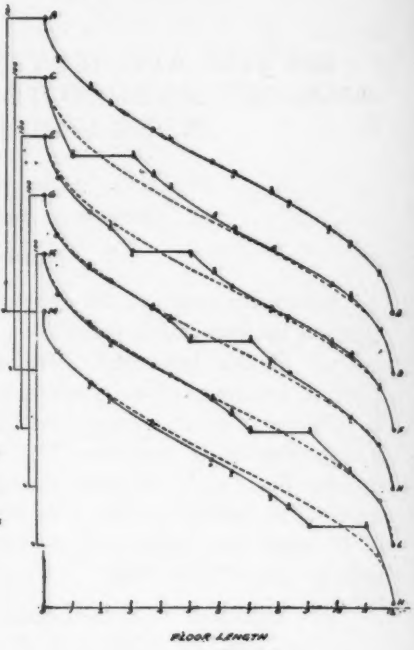


FIG. 3

Observations of pressure distribution under the floor were taken with 7 cm. and 4 cm. heads of water. The effect of the cavity in five different positions has been investigated.

Having obtained the pressure distribution in the hydraulic model an analogous electrical model was set up.

The Electrical Model.—It consists of a shallow elliptical tray 50″ long and about 3″ deep provided with ground glass bottom. The electrical analogue of the upstream and downstream levels is given by two thick copper plates AB and CD shown in Fig. 2.

These plates are maintained at an electrical potential difference corresponding to the hydraulic head of water. The portion BC is made up of an ebonite strip placed flush with the face of the copper strips AB and CD. BC is 12″ long and corresponds to the impervious floor. The cavity in the electrical case is provided by a semi-cylindrical piece of solid brass 2″ in diameter and about 2·5″ long. The cavity was fixed against the ebonite plate in exactly similar positions as was done in the hydraulic model. In order to measure the potential distribution, the tray was filled with water

to serve as an electrolyte. A neon tube oscillator with a valve amplifier was employed as the source of A.C. Potential along the floor was measured on a potentiometer by means of a probe and a headphone as shown in Fig. 2.

Results

The percentage pressure distribution obtained both by the hydraulic model experiments and by the electrical method are plotted and shown in Fig. 3. Curve AB gives the pressure distribution for a flush floor without any cavity. The other curves CD, EF, GH, KL, and MN give the pressure distribution with five different positions of the cavity. The dotted curves superposed on CD, EF, etc., are the same as AB and enable a ready comparison of the change of pressure caused by the cavities in different positions. The position of the cavity is indicated by the portions of the curves which are parallel to the abscissa, because there is practically no fall of pressure or potential within the cavity.

It will be noticed that the curves of the electrical and hydraulic methods almost coincide, thus establishing the applicability of the electrical analogy method to the determination of pressure distribution under weirs with cavities.

The hydraulic method is very laborious and liable to errors whereas the electric method is quick and capable of greater facility and accuracy.

The weirs in the Punjab are provided with pressure pipes which are regularly observed. A departure from the normal pressure distribution in the pressure pipes is taken to indicate some abnormality such as a cavity in the subsoil. It is thus possible by comparing the pressures obtained in the prototype with the potentials obtained in an electrical model to determine the nature of the cavities under the floor.

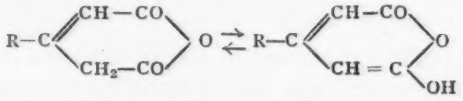
CHEMISTRY OF β ARYL GLUTACONIC ACIDS

Part VII. Constitution of the so-called Hydroxy-Anhydrides

By G. R. Gogte, M.Sc., Ph.D.

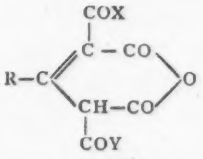
Received August 10, 1942
(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

The peculiar and outstanding property of the anhydrides of glutaconic acids containing a mobile hydrogen atom lies in their titratibility with alkalis and colourations with ferric chloride. Till now, the only theory proposed to account for these remarkable properties was the idea of hydroxy-anhydride—anhydride tautomerism, due to Thorpe[1],

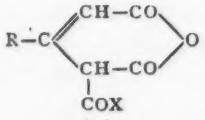


but this was unable to explain why it was not possible to prepare, with the exception of αβ dimethyl glutaconic anhydride, neutral acetyl or benzoyl derivatives of these bodies, although the corresponding chloro derivatives could be isolated in some cases.

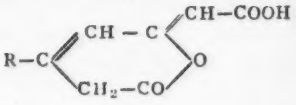
The systematic investigation of the acetylation and benzoylation of the β aryl glutaconic anhydrides by the present author,[2,3,4] led to the isolation of products which were proved to be C-acetyl or C-benzoyl glutaconic anhydrides (A). The alternative glutaconyl acetic acid constitution[5] (B), which Limaye and Bhave attempted so emphatically to defend[6], seems to



(C)



(A)



(B)

[1] Thole and Thorpe, *J.C.S.*, 1911, **101**, 2211.

[2] Gogte, *Proc. Ind. Acad. Sci.*, (A), 1938, 214.

[3] Gogte, *J. Univ. Bombay*, 1939, **8**, 208.

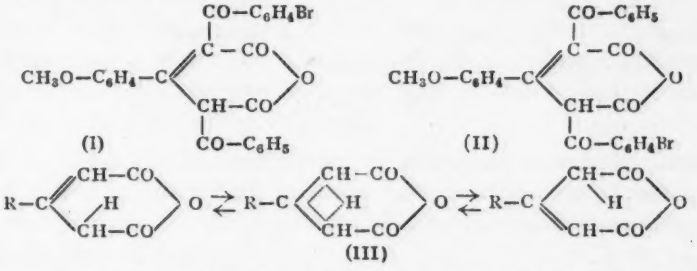
[4] Gogte, *ibid.*, 1940, **9**, 127.

[5] Limaye and Bhave, *ibid.*, 1933, **2**, 82.

[6] Bhave, *Rasayanam*, 1938, **1**, 127.

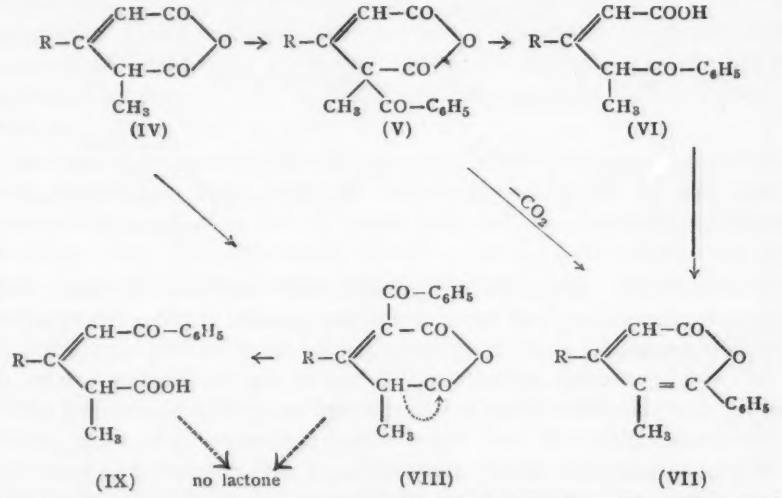
have lost its basis, especially after the publication of the work on the α-C-benzoyl-glutaconic anhydrides.

Einhorn's method, *i.e.*, the action of an acid chloride and pyridine, appears to be a simpler and more general method for the C-acylations of β aryl glutaconic anhydrides than the alternative Perkin's method. As Einhorn's method is known to yield generally the O-acyl derivatives, these α-C-acylations and especially the further αγ-C di-acylations to produce αγ-C-diacyl-glutaconic anhydrides of the types[3] (C), gave rise to a doubt as to the existence of a reactive hydroxy group in the β aryl glutaconic anhydrides. This indicated that the reactive hydrogen atom responsible for all the above reactions, instead of tautomerising to the neighbouring carbonyl group, wanders somewhere else. The apparent indentity of the α-C-benzoyl-γ-C-*p*. bromobenzoyl-β (4 methoxy-phenyl)-glutaconic anhydride (I) and the α-C-*p*. bromo benzoyl-γ-C benzoyl-β (4 methoxy-phenyl) glutaconic anhydride[4] (II) indicated a symmetrical tautomeric structure (III) for the β aryl glutaconic anhydrides, where the dotted lines represent half of the normal valency. Thus,



C-aroyl-β aryl- glutaconic anhydrides were observed to hold their aroyl groups tenaciously and hence it was not possible to prove the structure of the compounds (I) and (II) by transforming them into any derivatives of the α-C aroyl-glutaconic anhydrides. If one of the substituting groups at either the α or γ positions be an acetyl, it would easily be eliminated by acids[2] and the constitutions of αγ-C acetyl-bezoyl-glutaconic anhydrides could thus be established. The further acetylations of α-C benzoyl -β (4 methoxy-phenyl) glutaconic anhydride[4] or the benzoylation of α-C acetyl-β-(4 methoxy-phenyl) glutaconic anhydride[2], however, produced liquid reaction products which could not be purified by distillation, as they lost carbon-dioxide on heating. Solid αγ-alkoyl-aroyl-β aryl- glutaconic anhydrides may, however, be obtained in case different acid chlorides are tried with various glutaconic anhydrides but the work could not be proceeded with due to lack of materials.

A more simple and direct method for proving the identity of the α and γ positions in the β aryl-glutaconic anhydrides would be the study of the benzoylation of α-methyl- β aryl- glutaconic anydrides (IV). In case the α-position is attacked, the resulting α-C benzoyl derivative (V) would be neutral because of the absence of a mobile hydrogen atom. This derivative would, however, give a lactone (VII) by thermal decarboxylation or through the intermediate ketonic acid[2] (VI). If, however, the γ-position is attacked, the γ-C benzoyl derivative (VIII) would be acidic and give colouration with ferric chloride because of the presence of a mobile hydrogen atom. This γ-derivative would, however, give no lactone by either of the methods[4]. In case, however, the C- benzoyl- derivative of the α-methyl-β aryl-glutaconic anhydride titrates as an acid, gives a colouration with ferric chloride and at the same time yields a lactone by the usual methods, we are forced to the conclusion that the C-benzoyl-β aryl-glutaconic anhydride behaves at the same time as an α-benzoyl and γ-benzoyl compound, in other words the α- and γ- positions of α-methyl-β aryl-glutaconic anhydride are identical, and that the reactive hydrogen atom wanders between them.

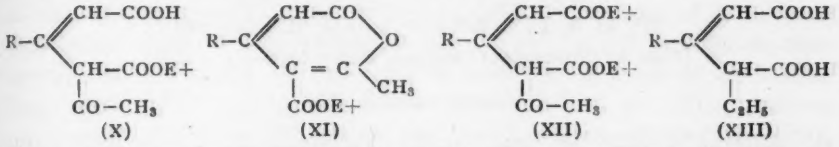


For the preparation of α-alkyl-β aryl-glutaconic acids, Thorpe and Wood's method[7] of alkylating the sodium derivative of diethyl-glutaconate by alkyl-halides was employed by Limaye and Bhave[8] in the case of diethyl-β (4methoxy-phenyl)-glutaconate. On repeating the work of Limaye and Bhave, the present author was unable to isolate any α-methyl

[7] Thorpe and Wood, *J.C.S.*, 1913, **103**, 1569.

[8] Limaye and Bhave, *Rasayanam*, 1939.

derivative. The reduction of the acid-ester[2] (X) to the α-ethyl-β (4 methoxy-phenyl) glutaconic acid (XIII) could not be effected as each time the lactonic ester (XI) resulted. To prevent this, the further esterification of this acid ester was attempted; the resulting di-ester (XII) could easily be reduced by Wolff's method[9] selectively to give the α-ethyl-glutaconic acid (XIII). All attempts at this esterification, even by the specific silver salt-ethyl iodide method, yielded the lactonic ester (XI) instead.



A third way for preparing the α- alkyl β aryl-glutaconic anhydrides was the condensation of α-methyl-acetone-dicarboxylate with phenolic ethers, and identifying the resulting αβ and βγ isomers of the resulting β aryl-glutaconic acids by ozonisation. (Compare Kon *et el.*) It was, however, found that at lower temperatures, the α methyl-acetone-dicarboxylate does not condense with phenolic ethers in the presence of sulphuric acid, whereas at higher temperatures it itself gets decomposed. The only way now open thus is to try the benzoyalation of any known di-substituted glutaconic anhydride, but the work was held up due to lack of materials and is a problem for future research.

Thus although, the constitution of glutaconic anhydrides cannot be said as definitely established, methods have been discovered which would settle the question one way or other, and several new facts have been noticed during the investigation.

Thus,

(1) The C-acylation of anhydrides of dibasic acids is shown to take place for the first time.

(2) The αγ-C diacylation of β aryl glutaconic anhydrides is peculiar, and this leads to a general method for synthesising several diphenyl derivatives.

(3) The isomeric transformation of the α-C-acetyl-β-aryl glutaconic anhydrides into the lactoric esters, by dilute sulphuric acid is remarkable.

(4) The thermal decarboxylation of α-C- acyl- β aryl glutaconic anhydrides to produce the corresponding lactones is strange and more work is necessary to elucidate the exact nature of the reaction, although a probable explanation has been suggested.[4]

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[9] L. Wolff, *Ber.*, 1911, **44**, 2769 ; *Annalen*, 1912, **394**, 86.

RAMAN EFFECT AND HYDROGEN BONDS

Part VI. Chelate Compounds: Esters of Salicylic Acid and their Mixtures

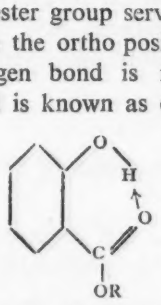
By G. V. L. N. Murty and T. R. Seshadri

(From the Department of Chemistry, Andhra University, Waltair)

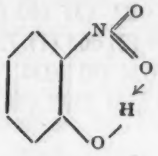
Received August 18, 1942

In previous papers of this series[1] investigations on intermolecular hydrogen bonds formed between molecules of different kinds and of the same kind were described. It has been found that the formation as well as the stability of the hydrogen bonds depend mainly upon the chemical constitution of the molecular species involved. In this paper it is proposed to describe experiments relating to a few substances containing intramolecular hydrogen bonds and their mixtures with typical solvents. The procedure adopted has already been described; the changes brought about in the C=O frequency of carbonyl compounds are followed under different conditions.

As the most suitable substances the esters of salicylic acid have been selected. The C=O of the ester group serves as the donor centre and the phenolic hydroxyl situated in the ortho position acts as the acceptor group with the result that hydrogen bond is readily formed. This type of intramolecular hydrogen bond is known as chelate bond.



The study of chelation originated with the peculiar behaviour of nitrophenols observed by Auwers and Orton.[2] They noticed that while meta and para nitrophenols gave abnormally high values for their molecular weights ortho nitrophenol was normal. This has been explained as due to the existence of association in the first two compounds by means of intermolecular hydrogen bonds and to the impossibility of association in the ortho compound due to internal hydrogen bond formation as below:



The work of Sidgwick[3] and his collaborators relating to physical properties such as solubility, volatility, etc., of a large number of benzene derivatives has been mainly responsible for our present definite knowledge of the subject of chelation. More recently Hilbert, Hendricks and Liddel[4] have shown that the infra-red absorption method could be used for the study of chelation. They found that the absorption in the vicinity of 1·46 to 1·60 μ which is characteristic of NH or OH groups was absent in such well-known chelate compounds as salicylaldehyde, O-hydroxy acetophenone, methyl salicylate, O-nitrophenol, etc. It was shown by Freymann[5] using the same method that rise of temperature has no effect on intramolecular hydrogen bonds. The Raman spectra of the above compounds have also been studied by other workers[6] who have attributed the abnormally low C=O frequencies of these compounds (as compared with those having no hydroxyl group in the ortho position) to the existence of the chelate bond. It, therefore, comes under the category of true hydrogen bonds in which both anionoid and cationoid centres are affected by the linkage.

The Raman spectra of (1) methyl salicylate, (2) ethyl salicylate, (3) *n*-butyl salicylate, (4) isoamyl salicylate and (5) phenyl salicylate (molten condition) were studied after careful purification by distillation under reduced pressure. Of these (3) and (4) have been examined for the first time and the others reinvestigated. The frequencies recorded are given below:

Methyl salicylate.—142 (2) 187 (3) 266 (3) 360 (3) 443 (3) 514 (2) 565 (6) 669 (1) 812 (10) 849 (2) 877 (2) 1036 (8) 1139 (2) 1160 (2) 1192 (2) 1253 (6) 1335 (8) 1442 (3) 1465 (5) 1477 (1) 1582 (2) 1615 (3) 1679 (8b) 1722(1)*

Ethyl salicylate.—162 (2) 252 (2) 307 (2) 450 (4) 508 (1) 563 (8) 669 (2) 754 (1) 781 (1) 816 (8) 857 (7) 975 (2) 1033 (9) 1113 (1) 1136 (2) 1156 (2) 1190 (1) 1247 (10) 1326 (9) 1374 (2) 1400 (2*b*) 1464 (6*b*) 1585 (3) 1611 (4) 1676 (8*b*) 1724 (1)*

n-*butyl salicylate.*—438 (1) 453 (1) 527 (1) 565 (8) 665 (1) 764 (0) 818 (3) 845 (2) 1036 (5) 1137 (2) 1156 (2) 1199 (1) 1252 (10) 1329 (4) 1400 (3*b*) 1471 (4) 1586 (3) 1612 (4) 1674 (8*b*) 1721 (1)*

Isoamyl salicylate.—443 (1) 460 (1) 567 (8) 668 (3) 712 (2) 763 (3) 815 (5) 829 (2) 874 (1) 1033 (8) 1136 (3) 1157 (3) 1253 (10) 1326 (5) 1403 (5*b*) 1468 (6*b*) 1586 (3) 1616 (4) 1676 (8) 1721 (1)*

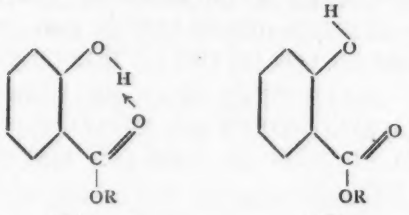
Phenyl salicylate (*molten*).—92 (3) 163 (3) 187 (3) 243 (4) 436 (0) 470 (2) 506 (2) 528 (2) 561 (8) 614 (2) 665 (1) 753 (2*b*) 798 (1) 812 (1) 841 (3) 861 (1) 914 (0) 938 (0) 998 (8) 1024 (4) 1034 (4) 1064 (1) 1096 (1) 1125 (1) 1156 (3) 1191 (3) 1247 (4) 1333 (5*b*) 1392 (1*b*) 1463 (6*b*) 1581 (3) 1594 (3) 1615 (3) 1687 (6*b*) 1739 (1)*

The frequencies marked * are recorded for the first time and their significance is discussed in this paper.

The C=O frequencies alone are collected in the following table:—

	Methyl salicylate	Ethyl salicylate	*n*-Butyl salicylate	Isoamyl salicylate	Phenyl salicylate
Bright line	1679	1676	1674	1676	1687
Faint line	1722	1724	1721	1721	1739
Difference in wave numbers	43	48	47	45	52

Thus there are two lines for each ester, the one with the lower frequency is stronger and the other with the higher frequency is very faint. The latter is a new line now noted for the first time and its existence seems to be highly significant. Further the first four esters derived from aliphatic alcohols have their frequencies almost the same, within the limits of experimental error, whereas those of phenyl salicylate are higher. This is in line with our observations with other phenyl esters.[7] The lower frequencies of the bright C=O lines, also observed by earlier workers are attributed to chelation. It is now suggested that the new faint lines are due to the existence of small proportions of the ester molecules in which the chelate bonds do not exist and that there is an equilibrium between the two molecular types (A and B) in the liquids, type B being very small in amount.



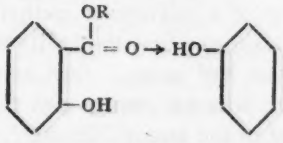
(A) (B)

In support of this interpretation may be mentioned (1) the higher frequencies correspond to the C=O frequencies in the related compounds, methyl benzoate (1720), ethyl benzoate (1720) and phenyl benzoate (1740) in which the C=O groups are unco-ordinated owing to the non-existence of ortho hydroxyl groups and (2) the analogy between this

and the weak C = O lines of acetic acid which arise from a small proportion of open dimers existing in equilibrium with the ring types. In this connection it may be relevant to recall the explanation offered by Pauling[8] for the existence of two hydroxyl absorption peaks in the infra-red spectra of ortho chlorophenols observed by Wulf and Liddel[9]. He postulated the presence of *cis* and *trans* forms existing in equilibrium, the *cis* being obviously in the chelate condition. It is quite possible that in the case of the chlorophenols more of the *trans* form exists than in the case of the carbonyl compounds. From the results recorded above it is clear that the phenomenon is more or less universal in chelate compounds.

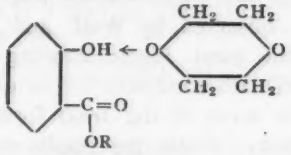
With regard to the chelate bond it may be stated that it is a fairly strong one since the lowering of the C=O frequency due to it is round about 46 wave numbers for the first four esters and somewhat higher for phenyl salicylate. The variation in strength is very little since the groups involved are practically the same all through. Still the existence of the influence of the groups is evident from the small difference noted in the case of phenyl salicylate. Other cases that have been studied, but not yet published, seem to confirm the general proposition[10] that the strength of the hydrogen bond depends upon the donor and acceptor groups and that it holds good even in the case of chelate bonds.

Mixtures.—In order to get more information regarding the chelate bond the spectra of mixtures were obtained using methyl and ethyl salicylate as one component and various donor and acceptor liquids as the other. Admixture with chloroform was found to produce no changes. Since this solvent is not strong in its capacity as a cationoid reagent, phenol was next used. Even in this solvent the C=O lines of the salicylates were unaffected thereby indicating that no change had taken place. It may be argued that though there may be a change it may not be observable since the new intermolecular H bonds are also between an ester C=O and a phenolic hydroxyl and hence may closely resemble the chelate bond.



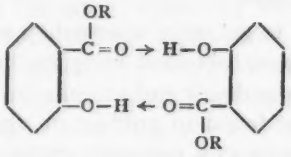
But this is not right for the reason that the intermolecular hydrogen bond between ethyl benzoate and phenol causes a lowering of only 20 wave numbers in the C=O frequency and a similar bond could, therefore, be distingushed from the chelate bond. As a typical donor solvent and also the most convenient one, dioxan was next employed. In analogy with its behaviour

with acetic acid[11] it could be expected to attack the hydroxyl centre as represented below and render the C=O groups free, thereby causing the higher C=O frequency to brighten up.



No such changes in the C=O frequencies were noticed in the mixture. It may, therefore, be concluded that the chelate bonds are strong and hence remain unaffected by these solvent molecules. Herein lies a marked difference between these chelate bonds and the intermolecular type of hydrogen bonds which are susceptible to be broken up. But this statement should be strictly taken for the present to apply only to the salicylates since other chelate bonds have yet to be studied in detail.

At this stage another point may also be dealt with. The fact that the salicylates have lower C=O frequencies is also capable of being explained by the possibility of their existing as bimolecular associates as shown below:



But this is unacceptable for many reasons, *viz.*, (1) the molecular weights correspond to single molecules, (2) such large rings involving twelve atoms may not be expected to be stable and (3) even if present they should be capable of easy break down (just as other ring dimers) by solvents like phenol and dioxan, thus leading to the brightening up of the higher C=O frequency.

The Raman Spectrum of a mixture of methyl salicylate and acetic acid (1 : 1) was also taken. It showed that the 1670 cm.$^{-1}$ line of the acid and the 1679 cm.$^{-1}$ line of the ester had merged into one and a bright broad line resulted. Otherwise there was no change and the faint lines of the acid (1710 and 1745 cm.$^{-1}$) and of the ester (1722 cm.$^{-1}$) were unchanged. In our work relating to the study of mixtures of acetic acid with esters it was shown that the esters produce marked change owing to their capacity to act as anionoid solvents. They brighten up the weak lines and reduce the intensity of the bright line at 1670 cm.$^{-1}$ The salicylates are obviously exceptional owing to the fact that the ester C=O is already locked up in

a stable chelate bond. Further, from this experiment it could also be concluded that the acetic acid molecules are incapable of being affected by the phenolic hydroxyl of this ester which also cannot function. Thus salicylates are not only unaffected by other solvents (donor or acceptor) but are incapable of affecting other susceptible liquids containing hydrogen bonds.

Summary

The Raman spectra of methyl, ethyl, *n*-butyl, iso-amyl and phenyl esters of salicylic acid have been studied. Besides the bright frequency attributable to the C=O group of the chelate structure, a weaker line corresponding to the unchelate molecule has been observed in each case. Thus the liquids contain the two types existing in equilibrium, the chelate molecules being predominant. The extent of the lowering of the C=O frequency brought about by chelation indicates that this type of intramolecular hydrogen bond is strong. This is also supported by the study of the mixtures of methyl and ethyl salicylates, with chloroform, phenol, dioxan and acetic acid. The spectra are unaffected showing that the chelate bond cannot be broken by anionoid and cationoid solvents and that salicylates cannot function as other esters and phenols do in breaking down hydrogen bonds.

REFERENCES

1. Murty and Seshadri .. *Proc. Ind. Acad. Sci.*, (A), 1941, **14**, 593 ; 1942, **15**, 154, 230, 238 ; 1942, **16**, 50.
2. Auwers and Orton .. *Z. Phys. Chem.*, 1896, **21**, 337.
3. Sidgwick and Callow .. *J. C. S.*, 1924, **125**, 527 (References to 14 earlier papers are given in this paper).
4. Hilbert, Hendricks and Liddel *Nature*, 1935, **135**, 147.
5. Freymann .. *J. Phys. Radium*, 1939, **10**, 1.
6. Among the notable ones the following may be mentioned :—
   Kohlrausch *et al.* .. *Wien. Ber.*, 1935, **144**, 448.
   Matsuno and Han .. *Bull. Chem. Soc. Japan*, 1939, **9**, 88 ; and
   Bonnino *et al.* .. *Rec. Sci.*, 1939 (ii), 8, Rep. I to IV.
7. Murty and Seshadri .. *Proc. Ind. Acad. Sci.*, (A), 1939, **10**, 307.
8. Pauling .. *J. A. C. S.*, 1938, **58**, 94.
9. Wulf and Liddel .. *Ibid.*, 1935, **57**, 1464.
10. Murty and Seshadri .. *Proc. Ind. Acad. Sci.*, (A), 1941, **14**, 593.
11. ———— .. *Ibid.*, 1942, **16**, 50.

RAMAN EFFECT AND CHANGE OF STATE: NAPHTHALENE

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1. Introduction

The comparative study of the Raman spectra of the same substance in different physical states (*i.e.*, vapour, liquid, amorphous solid, crystal) offers a fruitful field of research, as the data furnished by it help in elucidating the nature of the differences between these states and the conditions in which the transformations between them occur. The differences between the spectra are particularly conspicuous in the region of the smaller frequency shifts ascribable to the movements of translation or rotation of the molecules or ions composing the substance, the characters of such movements being naturally very different in the several states of aggregation. Not less important, though not so obvious, are the changes in the spectra appearing in the region of larger frequency shifts where we are concerned with the internal vibrations of the molecules or ions. These changes may involve the appearance or non-appearance in the spectra of particular modes of vibration, differences in the magnitude of the frequency shifts, as also differences in the character of the spectral lines, *viz.*, their width or multiplicity, their intensity and their state of polarisation. For the full and correct appreciation of these differences, it is clearly necessary that the comparative study should be made under similar experimental conditions. Especially for the observation of small changes in the frequency shifts, or of changes in the width or intensity of the spectral lines, is it necessary that the studies should be of a critical character. It is not easy to decide upon the reality of such changes by comparing the results reported by different investigators, since instrumental, experimental and personal factors may influence these to a not negligible extent. Even the results obtained by the same investigator with the same instrument but with the spectra recorded and measured separately are not entitled to the same degree of confidence as a direct comparison of the spectra in two physical states in which they are photographed with the same instrument and *on the same plate side by side with a Hartmann diaphragm* under similar experimental conditions. As an illustration of the

possibility of obtaining new and valuable results by such a procedure, it is proposed in this paper to record the results of a comparison of the spectra of naphthalene in the state of a crystal and in the molten condition.

2. Experimental Arrangements

To obtain the spectrum of liquid naphthalene, the substance was purified by double distillation in vacuum. The material thus purified was held in a cylindrical glass tube and kept in molten condition a few degrees above the temperature of fusion by surrounding the tube with an electrical heater and adjusting the current suitably. The spectrum of the solid was obtained with a small piece of transparent naphthalene crystal which was protected from evaporation by microscope cover slips stuck on its surfaces with a trace of Canada balsam.

A Hilger two-prism glass spectrograph of large light-gathering power and having a dispersion of about 21 Å per mm. in the 4046 Å region of the spectrum was employed for the study. The light of a mercury lamp was focussed by a lens of large aperture on the molten naphthalene and on the crystal respectively. The spectra of liquid and solid were recorded in succession on the same plate, using the two adjacent apertures of the Hartmann diaphragm covering the slit of the spectrograph. By preliminary trials, the exposures for solid and liquid were so adjusted as to give spectra of about the same intensity. An iron arc comparison spectrum was also recorded on the plate using the outermost aperture on the diaphragm, thus enabling the frequency shifts to be evaluated accurately.

3. Experimental Results and Discussion

Fig. 1 (*a*) and 1 (*b*) of Plate IX reproduce two spectra thus recorded side by side with molten and crystalline naphthalene respectively. The reproductions show the part of the spectrum excited by the 4046 Å line of the mercury arc. It will be seen on comparing the spectra that almost all the Raman lines have suffered displacements in passing from the solid to the liquid state. These displacements are different for the different lines and it is interesting to note that they are not all in the same direction, for some lines being an increase and for others a decrease of the frequency shift. Almost all the Raman lines for the crystal are sharp, while the corresponding lines in the liquid are usually more diffuse.

In Table I are given the results of careful measurements of the frequency shifts as well as also the measured displacements of the Raman lines in passing from solid to liquid and the direction of this displacement. The intensities of the several lines are recorded relatively by visual estimate.

The intensities of the lines for the crystal, however, depend on its orientation which in this case was undetermined. As neither the illuminated volumes nor the exposure times were identical, the present research does not tell us anything about the intensity changes of the Raman lines in the act of melting. It is evident, however, that the relative intensities of the lines do not always remain the same in the solid and liquid states.

TABLE I

Raman Spectra of Naphthalene

Frequencies expressed in cm.$^{-1}$			Frequencies expressed in cm.$^{-1}$		
Molten	Single crystal	Relative shift, positive or negative	Molten	Single crystal	Relative shift, positive or negative
Wing with a frequency limit 93	43 (10)		1193 (1)	1192 (2)	−1
	73 (20)		1206 (½)	1206 (1)	0
	105 (15)			1226 (½)	
	121 (8)		1238·5 (½)	1240·5 (1)	2
194 (½)			1254 (½)	1250 (½)	−4
382·5 (½)	388 (2)	5·5	1302 (1)	1302 (2)	0
409 (1)	406 (3)	− 3		1325 (1)	
470 (1)	466·5 (3)	− 3·5	1374 (15)	1378·5 (15)	4·5
508 (9)	508·7 (10)	0·7	1440 (2)	1442 (3)	2
726 (2)	725 (2)	− 1	1452·5 (8)	1456·5 (9)	4
731 (½)	737 (1)	6		1481·4 (1)	
758 (9)	761 (10)	3	1531 (½)	1528·5 (1)	−2·5
774 (2)	785 (2)	11	1571·5 (8)	1572·5 (9)	1
943·7 (2)	952 (3)	8·3		1625 (1)	
	973 (½)		3002 (1)	3004 (1)	2
1002 (½)	1003 (½)	1	3025 (3)	3026 (2)	1
1025 (9)	1016 (10)	− 9	3046 (3)		
1144 (2)	1144 (5)	0	3057 (8)	3053 (10)	−4
1160 (1)	1166·5 (2)	6·5	3246 (½)	3247 (½)	1

The Raman spectra of naphthalene has been studied by several authors whose names appear in the list of references given at the end of the paper. Naphthalene in the form of crystalline powder was studied by the authors cited in references 2, 1, 3, 8, molten naphthalene in references 12, 16, 5, 13 and solutions of naphthalene in some solvents in 4, 10, 9, 14. The Raman spectra of single crystals of naphthalene have been studied by Benel (1940) and Nedungadi (1941). On the spectrum of molten naphthalene, the report by Saxena is the most complete, while on the spectra of single crystals of naphthalene, the results of Nedungadi are the most exhaustive. Almost all the lines recorded by Nedungadi for the solid and for molten naphthalene by Saxena and a few additional lines besides hitherto unobserved are recorded in the present paper.

It may be remarked that in the spectrum of the melt, a line is observed corresponding to every line observed in the spectrum of crystal, except that the low frequency lines are replaced by a wing in the melt and that a few extremely weak lines recorded with the crystal are not noticed in the spectrum of the melt. There is a faint indication of the presence of a line at 194 in the spectrum of the melt as reported by Saxena. But there is definitely no line corresponding to this in the solid. Five lines are observed in the spectrum of the melt which are ascribable to the CH oscillations. Amongst these, the line at 3046 which appears as a sharp component of 3057 does not appear in the spectrum of the crystal. The other four lines are also found in the crystal though in slightly shifted positions. The weak line at 3246 observed by Saxena and whose presence in the solid was doubted by Nedungadi is found to appear both in the melt and in the solid.

The displacements of the frequencies of the corresponding lines in going from the solid to the liquid state of naphthalene have been directly measured on the plate, and both their direction and their magnitude as given in the table may therefore be considered trustworthy. Though the lines in the crystal in general are sharp and intense compared with the lines in the melt, the latter being usually weaker and more diffuse, a few of the lines such as 944, 1254, 1452 and 1571 are sharper in the melt than in the crystal. The line 1374 appears to be more intense in the melt than in the solid, but this may be the result of the particular orientation of the crystal specimen. In the vicinity of the line with frequency shift 1571 in the melt, another line appears clearly separated from it in the spectrum of the melt, while it is not seen so clearly in the solid, being only just separated from the 1572 line in the solid. This is however not a distinct frequency shift, being due to excitation by the 4077 Å line of the mercury arc of the frequency shift 1374 in the liquid and the 1378 in the solid.

It will be seen from Fig. 1 in Plate IX and from the measurements recorded in the table that the wing for the melt extends only to 93 cm.$^{-1}$ whereas the last of the lattice lines goes up to 128 cm.$^{-1}$ Further, the distribution of intensity in the wing is different from that of the lattice lines of the crystal. Thus, the description given by Gross and Vuks (1935) of the change on melting, namely that the lattice lines of a crystal broaden and merge with each other, thereby going over to the " wing " observed with the liquid does not correctly represent the actual facts. Indeed, as has already been remarked by Nedungadi, the phenomena observed with naphthalene give no support to the hypothesis of a quasi-crystalline structure of the liquid state.

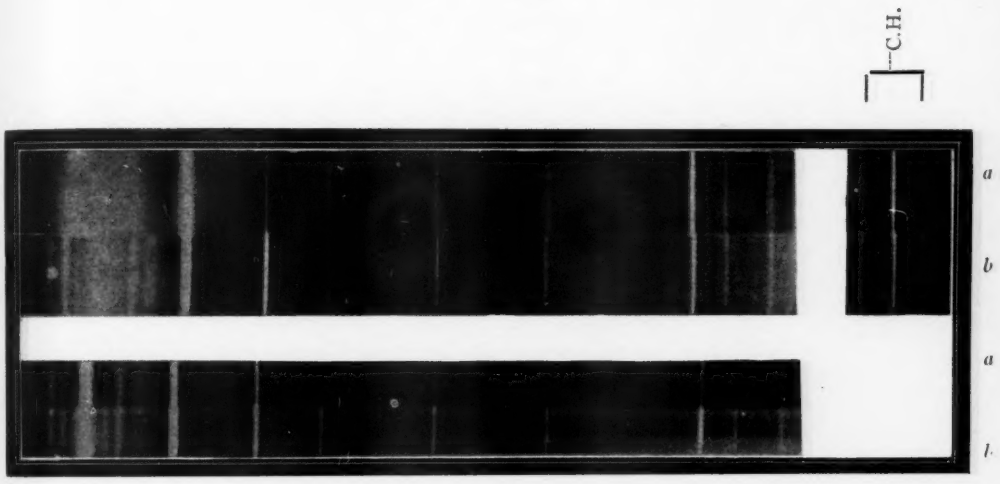
4. Spectra of the Crystal in Different Orientations

As a further illustration of the usefulness of the present procedure, a comparison has also been made of the Raman spectra with different orientations of a piece of naphthalene crystal cut perpendicular to the axes α, β, γ of the optical polarisability ellipsoid. Exposures were made successively on the same plate with the aid of a Hartmann diaphragm, the crystal being differently orientated each time with reference to the directions of incidence of the light and the direction of observation of the scattered light. Fig. 2 in Plate IX reproduces two of the spectra thus recorded, the actual setting of the crystal being indicated in each case. Striking changes in the relative intensities of several of the lines in the two spectra will be noticed. The frequency shifts in the two spectra do not however exhibit the same striking differences as between solid and liquid. Nevertheless many of the lines on careful examination do give indications of displacement as between the two spectra; for the lines 509, 952 and 1456, this is in the increasing direction in passing from to 1 to 2, while for 761, 1016, 1378 and 1572 there is a shift in the decreasing direction which is particularly distinct for the line 1572. That displacements of this kind are to be expected theoretically has already been pointed out by Nedungadi. In his polarisation studies he has already recorded the splitting of the lines with frequency shifts 43, 509 and 1576.

In conclusion, the author desires to record his respectful thanks to Prof. Sir C. V. Raman for his invaluable suggestions and kind encouragement during the course of this work.

5. Summary

The paper briefly reports a study of the changes of the Raman spectra of naphthalene in the transition from the solid to the liquid state which become evident when the spectra are recorded with the same instrument and on the same plate adjacent to each other by using a Hartmann diaphragm. It is found that almost all the Raman lines undergo relative shifts of varying magnitudes and that this shift is in one direction for some lines and in the other direction for the others. Changes in intensities of the corresponding lines in the two cases are also observed. Incidentally the paper also records more complete spectra of the naphthalene crystal and of the melt than have been reported earlier. In general, almost every line other than the lattice lines, appears both in the melt and the solid. Observations have also been made of the spectra of the naphthalene crystal similarly recorded side by side for two different orientations. Besides the changes in intensities of the several lines, relative shifts of their positions are



Raman Spectra of Naphthalene

			I.L.	S.L.	⊙
Fig. 1 *a*.	Naphthalene	Molten			
b.	„	Crystal			
Fig. 2 *a*.	Naphthalene	Crystal	$\rightarrow\beta$	$\downarrow\gamma$	α
b.	„		$\rightarrow\beta$	$\downarrow\alpha$	γ

observed though small in comparison with those found in the transition from solid to liquid.

REFERENCES

1. Ananthakrishnan .. *Proc. Ind. Acad. Sci.*, 1937, **5**, 200.
2. Bär .. *Nature*, 1929, **124**, 692.
3. Canals and Peyrot .. *Comptes Rendus*, 1938, **206**, 1179.
4. Dadieu and Kohlrausch .. *Wien. Ber.*, 1929, **138**, 335.
5. Gockel .. *Z. f. Phys. Chem.*, 1935, **29**, 79.
6. Gross and Vuks .. *J. Phys. Radium*, 1936, **7**, 113 ; *Nature*, 1935, **135**, 100, 431, 998.
7. Hilmi Benel .. *Theses*, Bordeux, 1940.
8. Kohlrausch .. *Z. f. Phys. Chem.*, 1938, **31**, 431.
9. Manzoni .. *La. Recerca Sci.*, 1936.
10. Mutsuno and Han .. *Bull. Chem. Soc. Japan*, 1936, **11**, 321.
11. Nedungadi .. *Proc. Ind. Acad. Sci.*, 1941, **13**, 161 ; 1942, **15**, 396.
12. Petriikaln and Hochberg .. *Z. f. Phys. Chem.*, 1929, 217.
13. Saxena .. *Proc. Ind. Acad. Sci.*, 1938, **8**, 73.
14. Sirkar .. *Ind. Journ. Phys.*, 1936, **10**, 109.
15. Venkateswaran .. *Proc. Ind. Acad. Sci.*, 1938, **8**, 448.
16. Zeimecki .. *Z. f. Phys.*, 1932, **78**, 123.

ORDERED GROUPS

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The theory of ordered fields has a kind of counterpart in the theory of ordered groups. Every element $\neq 1$ of an ordered group is necessarily of infinite order. This condition being satisfied Abelian groups as well as every group* the commutator-group of which is situated in the centre, can be ordered. In general, the order is of a non-Archimedean type. Those elements which in Archimedean sense are either comparable with a particular element a or infinitely small to a form a group A; the latter class of elements form a normal subgroup E. The group A/E will be proved to be an abelian group which is isomorphic to a module of real numbers every coset of E in A being characterised by a real number $\lambda = {}_a\lg(b)$ which has the character of a logarithmus to the base a. As the groups considered in this paper are not necessarily abelian, the multiplicative language is used, and the unitelement is denoted by 1. With regard to the terms "positive" and "negative", the notation O would have some advantage.

§1. Suppose a group G is partitioned into two sets $\mathbf{S}$ and $\mathbf{S}'$ satisfying the following conditions.

1. $\mathbf{S} \vee \mathbf{S}' = G$, $\mathbf{S} \wedge \mathbf{S}' = 1$.
2. $\mathbf{S}$ is a semi group and normal invariant in G ($g\mathbf{S}g^{-1} = \mathbf{S}$).
3. If b belongs to $\mathbf{S}$ (to $\mathbf{S}'$) then b^{-1} belongs to $\mathbf{S}'$ (to $\mathbf{S}$).

The order is established in G by the following definition.

If $ab^{-1} \neq 1$ belongs to $\mathbf{S}$, then $a > b$ (1)

" " $\mathbf{S}'$, " $a < b$.

Hence

either $a = b$, or $a > b$ or $a < b$ holds. (2)

* In a recent paper, the author has investigated groups of this kind from a different point of view. See "Groups in which the commutator-operation satisfies certain algebraic conditions," *Jour. Ind. Math. Soc.*, **6**, p. 87–97.

The notations $\geq$ and $\leq$ are used in the customary manner. An element a belongs to **S** or to **S'** according as $a \geq 1$ or $a \leq 1$ holds. The elements > 1 are called *positive*, the elements < 1 *negative* elements. The absolute value $|a|$ of a is defined by

$$\begin{aligned} |a| &= a \quad \text{if } a \geq 1 \\ |a| &= a^{-1} \text{ if } a \leq 1. \end{aligned} \tag{3}$$

If $a > b$, then $b < a$ and conversely;

$$\text{moreover } b^{-1} > a^{-1},\ ac > bc,\ ca > cb,\ b^{-1}a > 1. \tag{4}$$

$$a \geq b \text{ and } b \geq c \text{ imply } a \geq c \tag{5}$$

where the sign $=$ holds in the third inequality if and only if it holds in *both* the suppositions.

$$a > a' \text{ and } b > b' \text{ imply } ab > a'b'. \tag{6}$$

Suppose on the other hand that relations $>$ and $<$ are defined in G in such a way that (2), (4), (5) and (6) hold, then the system S of the elements ≥ 1, and the system S' of the elements ≤ 1 satisfy the conditions 1, 2 and 3. For the absolute values of a product, the following formulas can easily be shown

$$\begin{aligned} |ab| &= |a|\ |b| \text{ if } a > 1,\ b > 1 \\ &= |b|\ |a| \text{ if } a < 1,\ b < 1 \\ &= |a|\ |b|^{-1} \text{or} = |b|\ |a|^{-1} \quad \text{if } a > 1,\ b < 1 \\ &= |b|^{-1}|a| \text{ or} = |a|^{-1}|b| \quad \text{if } a < 1,\ b > 1; \end{aligned}$$

in the two last lines, the first or the second alternative holds true, according as $|a| > |b|$ or $|a| < |b|$.

Moreover $|a|^n = |a^n|$. For $a \neq 1$, $1 < |a| < \ldots < |a|^n = |a^n|$ holds. Hence a is of *infinite* order.

§2. Suppose that for two positive integral numbers **m** and **n**, and for two elements a and b of G the inequality

$$|a|^m \geq |b|^n \tag{7}$$

holds, then there are two possibilities. Either (7) holds for every pair of positive integrals **m** and **n**, then $|b|$ is said to be *infinitely small* to $|a|$, and this statement is denoted by

$$|a| \gg |b| \text{ and } |b| \ll |a|. \tag{8}$$

Or there exists a pair of positive integrals m', n' for which

$$|a|^{m'} < |b|^{n'} \tag{7'}$$

holds, then a and b are said to be *comparable*. Comparability will be denoted by

$$a \sim b. \tag{9}$$

Suppose that $a \sim b$, $b \sim c$, then $|b|^{\mathfrak{p}} > |c|^{\mathfrak{q}}$, $|b|^{\mathfrak{p}'} < |c|^{\mathfrak{q}'}$ holds for suitable positive integers $\mathfrak{p}$, $\mathfrak{q}$, $\mathfrak{p}'$ and $\mathfrak{q}$. Hence $|a|^{m\mathfrak{p}} > |c|^{n\mathfrak{q}}$ and $|a|^{m'\mathfrak{p}'} < |c|^{n'\mathfrak{q}'}$; thus $a \sim c$. Comparability is therefore a transitive property, and since it is also reflexive and symmetric, comparable elements of an ordered group form a class. For every $a \neq 1$

$$1 \lessdot |a|$$

holds; hence 1 forms a class by itself. If all the other elements are comparable, the order of G is of an *Archimedean* character. Similarly one shows that

$$|a_1| \geq |a| \gg |b| \geq |b_1| \text{ implies } |a_1| \gg |b_1|$$

and that

$$a' \sim a,\ |a| \gg |b|,\ b \sim b' \text{ implies } |a'| \gg |b'|.$$

§3. Let A be an abelian group in which every element $\neq 1$ is of infinite order. It will be proved that *A can be ordered.* An element a is said to be *dependent* on the elements $a_1, \ldots, a_m$ if for any $\mathfrak{n} \neq 0$, an equation

$$a^{\mathfrak{n}} = a_{\nu_1}^{\mathfrak{n}_1} \ldots a_{\nu_r}^{\mathfrak{n}_r} \tag{10}$$

holds. The exponents in (10) can be multiplied with any integral number, and can be divided by any common factor. Hence if $a \neq 1$ is dependent on $a_1, \ldots, a_m$, there exists a *canonical* form of the equation (10) where $\mathfrak{n} > 0$, $\mathfrak{n}_1, \ldots, \mathfrak{n}_\mu$ are all $\neq 0$, their *h.c.f.* is equal to **1** and the indices are ordered in the ascending order. A well ordered system

$$a_1, a_2, \ldots, a_\nu, \ldots\ldots \tag{11}$$

is said to be a *basis* of A if every element $\neq 1$ of A is dependent on a finite number of elements of (11) and if there exists only one canonical form of representation.

Given a basis (11) of A, and let

$$a^{\mathfrak{n}} = a_{\nu_1}^{\mathfrak{n}_1} \ldots a_{\nu_t}^{\mathfrak{n}_t}$$

be a canonical representation, then a is supposed to belong to $\mathbf{S}$ or to $\mathbf{S}'$ according as $\mathfrak{n}_1 > 0$ or $\mathfrak{n}_1 < 0$ holds; the element 1 is taken as a common element of $\mathbf{S}$ and $\mathbf{S}'$. The conditions 1, 2 and 3 of §1 are obviously satisfied, and therefore A is ordered.

It remains to prove† that A has a basis. As A is a group, it is also a set, and therefore it can be well ordered. Let

$$b_1, b_2, \ldots, b_\mu, \ldots \ldots \tag{12}$$

be the elements $\neq 1$ of A given as a well ordered set. Omit in (12) all those elements which are dependent on the preceding ones, the remaining set is non-empty (since it contains b_1) and well ordered; denote it by (11). There cannot be any relation $a_\rho^{\rho} \ldots a_s^{\sigma} = 1$ with exponents $\neq 0$, otherwise the a with the highest index is dependent on a's with lower indices, contrary to the supposition that no element (11) depends on elements which precede it. On the other hand every element (12) can be shown to depend on the elements (11). If not so, there is amongst the elements not depending on (11) one with a lowest index, say b_μ. Since b_μ is not an element (12), it depends on elements which precede it and which therefore are dependent on the elements (12). Hence b_μ depends on the elements (12). Suppose now that any b admits two different canonical representations, say

$$b^n = a_{\nu_1}^{n_1} \ldots a_{\nu_s}^{n_s} \qquad \nu_1 < \ldots < \nu_s$$

$$b^m = a_{\mu_1}^{m_1} \ldots a_{\mu_t}^{m_t}, \qquad \mu_1 < \ldots < \mu_t, \text{ then}$$

$$a_{\nu_1}^{mn_1} \ldots a_{\nu_s}^{mn_s} a_{\mu_1}^{-nm_1} \ldots a_{\mu_t}^{-nm_t} = 1.$$

Hence all the exponents are all zero, *i.e.*, $\nu_i = \mu_i$, $\mathrm{mn}_i = \mathrm{nm}_i$, for $\mathrm{i} = 1, \ldots,$ $\mathrm{s} = \mathrm{t}$, and that is impossible when the two canonical representations are different. Hence (11) is a basis of A.

§4. Let $\mathbf{Y}$ be a subset of an ordered group G with the property that if a belongs to $\mathbf{Y}$, then also a^{-1} and all the elements situated between a and a^{-1} belong to $\mathbf{Y}$; then $\mathbf{Y}$ will be called a *symmetric section* of G.

Let $\mathbf{Y}$ be a symmetric section of G and be a subgroup of G; if y belongs to $\mathbf{Y}$, whereas c is an element of G not belonging to $\mathbf{Y}$, then $| y |^{\mathbf{n}} < | c |^{\mathbf{m}}$ for every pair of positive integers $\mathbf{m}$ and $\mathbf{n}$. Hence

$$| y | \ll | c |. \tag{13}$$

On the other hand, let c be any particular element of G, then the elements y satisfying (13) form a symmetric section $\mathbf{Y}$ of G which is also a subgroup of G. If a does not belong to $\mathbf{Y}$, then either a is comparable with c, or $| c | \ll | a |$, hence (13) remains true if c is replaced by any element which does not belong to $\mathbf{Y}$. If in particular $a \sim c$, then every element y satisfying $| y | \ll | a |$, satisfies also (13).

† For the convenience of the reader the proof is given in full.

Given an element a; the elements which are comparable with a and those of which the absolute value is infinitely small to $|a|$ form together a symmetric section A which will be proved to be a *subgroup* of G. Let α and β be two elements of A, say $|\alpha| \geq |\beta|$, then $|\alpha^{\pm 1}\beta^{\pm 1}|$ and $|\beta^{\pm 1}\alpha^{\pm 1}|$ are smaller than $|\alpha|^2$, and therefore these elements belong to A; hence A is a subgroup of G. The elements whose absolute values are infinitely small to A form a group which is a subset and therefore a subgroup, say E of A. It will be proved to be a *normal subgroup* of A. If an element b of A does not belong to E, then $b \sim a$, and therefore $|\epsilon|^n < |b|$ for every n and every element ϵ of E. Now $b|\epsilon| > b$ and therefore $\beta = b|\epsilon|b^{-1} > 1$. Hence $1 < \beta^n = b|\epsilon|^n b^{-1} < b|b|b^{-1} = |b|$. Thus $\beta \ll |b|$ belongs to E and the same holds for $\beta^{-1} = b|\epsilon|^{-1}b^{-1}$. Hence E is a normal subgroup of A.

The elements of G which by any homomorphism are mapped on 1 form a normal subgroup of G. If in particular the homomorphism is order-invariant, then this subgroup is a symmetric section. It follows therefore that when by an order invariant homomorphism, y is mapped on 1 and c is mapped on an element $\neq 1$, then $|y| \ll |c|$ holds. This statement admits two inverse propositions.

(1) Let G be ordered, and let a normal subgroup N of G be a symmetric section of G, then the homomorphism which maps N on 1 is order-invariant.

If a is an element of any coset of N in G and ϵ is an element of N, then $a\epsilon$ is positive or negative, according as a is positive or negative. Thus every coset of N contains either only positive or only negative elements of G. In the first case the coset is considered to be a positive element of G/N, in the second case as a negative one. By this definition the conditions 1, 2 and 3 of §1 are satisfied. The positive elements of G are mapped on the positive elements and on the unitelement of G/N and similarly for the negative elements. Hence the mapping is order-invariant.

(2) Let G/N be ordered and also N be ordered in such a way that by an inner automorphism of G the positive (negative) elements of N are transformed into positive (negative) elements of N, then the order in N can be extended to an order in G, and this order is invariant for the mapping $G \to G/N$.

Consider the elements of the positive (negative) cosets of G/N and the positive (negative) elements of N as the positive (negative) elements of G. Then the conditions 1, 2 and 3 of §1 as well as the last proposition are satisfied.

If in particular the elements $\neq 1$ of a group A as well as those of its factorgroup $A/C(A)$ are of infinite order and the commutatorgroup $C(A)$ lies in the centre of A, then every element of $C(A)$ remains invariant for the inner automorphisms of A. Thus one has only to give an order to the two abelian groups $C(A)$ and $A/C(A)$ to obtain an order in the group A.

§5. Suppose that $\mathbf{m} : \mathbf{n} > \mathbf{p} : \mathbf{q}$, and $a^{\mathfrak{p}} > b^{\mathfrak{q}}$, where $\mathbf{m}, \mathbf{n}, \mathbf{p}, \mathbf{q}$ are positive integers and a, b is a pair of positive elements of an ordered group G. Then $a^{mq} > a^{nq} > b^{np}$; hence $a^{m} > b^{n}$. If therefore a and b are positive comparable elements of G, they determine a Dedekind section say, ${}_a\lg b$ of the rational positive numbers to the effect that

$$a^{\mathfrak{p}} > b^{\mathfrak{q}} \quad \text{if } \mathbf{p} : \mathbf{q} > {}_a\lg b \tag{14}$$
$$a^{\mathfrak{p}} < b^{\mathfrak{q}} \quad \text{if } \mathbf{p} : \mathbf{q} < {}_a\lg b.$$

${}_a\lg b$ may be rational or irrational; if it is rational, say $\mathbf{s} : \mathbf{t}$, then $a^{\mathfrak{s}}$ might be greater or less than $b^{\mathfrak{t}}$, or the elements might be equal. The definition (14) can be extended to non-positive elements b (the " basis " a is always considered to be a positive element) by

$${}_a\lg \epsilon = 0, \text{ for } \epsilon \ll a \tag{14'}$$
$${}_a\lg (b^{-1}) = -\,{}_a\lg b.$$

The following formulas are immediate consequences of the definition. ${}_a\lg (a^{m}) = \mathbf{m}$, ${}_a\lg(b^{m}) = \mathbf{m}\,{}_a\lg b$, ${}_a\lg b > {}_a\lg c$ implies $b > c$,

$$\text{and for } b > 1,\ {}_a\lg b\ {}_\beta\lg a = \mathbf{1},\ {}_a\lg b\ {}_b\lg c = {}_a\lg c \tag{15}$$

In particular ${}_a\lg b = \mathbf{1}$ implies ${}_b\lg a = \mathbf{1}$, but from this relation it does not follow necessarily that a and b are equal.

This function ${}_a\lg(b)$ will be used now to investigate the groups A, E and A/E introduced in §4. By

$$a, b, c \ldots\ldots \quad \text{(with and without indices)} \tag{16}$$

the *positive* elements of A will be denoted which do not belong to E, whereas ϵ (with or without an index) denotes elements of E, and $\alpha, \beta \ldots$ denote arbitrary elements of A. Hence the lg-function exists for every basis (16) and every variable α, and there is

$${}_a\lg(b) > 0,\ {}_a\lg(b^{-1}) < 0,\ {}_a\lg(\epsilon) = 0.$$

Moreover $a^{\mathfrak{p}} \leq \alpha^{m} \leq a^{\mathfrak{q}}$ implies $\mathbf{p} : \mathbf{m} \leq {}_a\lg \alpha \leq \mathbf{q} : \mathbf{m}$ if $\mathbf{m}$ is positive.

When the group A is *abelian*, one can show easily that

$${}_a\lg \alpha\beta = {}_a\lg \alpha + {}_a\lg \beta. \tag{17}$$

The general validity of (17) will be proved now.

Since E is a normal subgroup of A, all the commutators (α, ϵ) belong to E. Hence

$$(\epsilon b)^n = \epsilon\,(b, \epsilon)\,\epsilon b^2\,(\epsilon b)^{n-2} = \epsilon_2 b^2\,(\epsilon b)^{n-2} = \epsilon_2\,(b^2, \epsilon)\,b^3\,(\epsilon b)^{n-3} =$$
$$= \epsilon_3 b^3\,(\epsilon b)^{n-3} = \ldots = \epsilon_n b^n.$$

Now $|\epsilon_n| < b$, hence $b^{n-1} < \epsilon_n b^n = (\epsilon b)^n < b^{n+1}$
for every positive integer $\mathbf{n}$. Hence ${}_b\lg(\epsilon b) = \mathbf{1}$

$${}_a\lg(\epsilon b) = {}_a\lg b$$
$$\text{and similarly } {}_a\lg(b\epsilon) = {}_a\lg b. \tag{18}$$

From (18) it follows that if ${}_a\lg a_1 \neq {}_a\lg a_2$,

$$a_1 = a_1 a_2^{-1} \cdot a_2 \neq \epsilon_1 a_2$$
$$= a_2 \cdot a_2^{-1} a_1 \neq a_2\,\epsilon_2 \cdot \text{ Hence}$$
$${}_a\lg(a_1 a_2^{-1}) \neq 0,\ {}_a\lg(a_2^{-1} a_1) \neq 0. \tag{19}$$

Let b run over all the elements (16); then two cases are distinguished.

1. Among the positive numbers ${}_a\lg b$ (where the basis a is kept constant) there is a smallest one.
2. To every a_n, there exists an element a_{n+1} such that $0 < {}_a\lg a_{n+1} < {}_a\lg a_n$ holds.

I. In the first case, one can interchange the elements (16) in such a manner that the minimum value of ${}_a\lg b$ is obtained for $b = a$. Hence ${}_a\lg b \geq 1$.

Suppose ${}_a\lg b = 1$, then for every α there is ${}_a\lg\alpha = {}_b\lg\alpha$.
Thus there is no loss of generality in supposing that $b < a$.
Since ${}_a\lg b^2 = \mathbf{2}$, $\quad a < b^2$;
hence $1 < b^{-1}a < b$, and therefore $1 < a\,b^{-1} < (ab^{-1})^2 = a \cdot b^{-1}a \cdot b^{-1} < a$
Therefore $0 \leq \mathbf{2}\,{}_a\lg(ab^{-1}) = {}_a\lg(ab^{-1})^2 < {}_a\lg a = \mathbf{1}$.
Hence ${}_a\lg(ab^{-1}) = 0$, $ab^{-1} = \epsilon$, $a = \epsilon b = b \cdot b^{-1}\epsilon b = b\epsilon'$.

On the other hand, a left or right hand factor ϵ does not change the value of the ${}_a\lg$ function. The elements b of A for which ${}_a\lg b = \mathbf{1}$ form therefore a coset of E. To every element α of A, there exists a (not necessarily positive) integral number $\mathbf{m}$, such that

$$\mathbf{m} \leq {}_a\lg\alpha < \mathbf{m} + 1. \text{ Hence}$$
$$a^{m-1} < \alpha < a^{m+1}$$
$$a^{-1} < \alpha\,a^{-m} < a \text{ and therefore } -1 \leq {}_a\lg(\alpha a^{-m}) \leq \mathbf{1}.$$

Hence ${}_a\lg\,(a a^{-m})$ can only have the values **1, 0, − 1** and correspondingly it is of the form $a\epsilon = \epsilon' a$, or ϵ, or $a^{-1}\epsilon_1 = \epsilon_2 a^{-1}$, and therefore

$$a = \epsilon a^{\mathfrak{p}}, \text{ where } \mathfrak{p} \text{ is any integral number, and}$$

from (18) it follows that ${}_a\lg a = \mathfrak{p}$. Let β be any other element of A, then $\beta = \epsilon' a^{\mathfrak{q}}$, ${}_a\lg\,\beta = \mathfrak{q}$. Hence $a\beta = \epsilon a^{\mathfrak{p}}\,\epsilon' a^{\mathfrak{q}} = \epsilon(a^{\mathfrak{p}}, \epsilon')\epsilon' a^{\mathfrak{p}+\mathfrak{q}} = \epsilon_1 a^{\mathfrak{p}+\mathfrak{q}}$.

Thus ${}_a\lg(a\beta) = \mathfrak{p} + \mathfrak{q} = {}_a\lg a + {}_a\lg\beta$.

II. Suppose that to every element a_ν of (16) there exists an element b such that $0 < {}_a\lg b < {}_a\lg a_\nu$ holds. If $b^2 \leq a_\nu$ then put $b = a_{\nu+1}$, but if $b^2 > a_\nu$, then

$$1 < a_\nu b^{-1} < b \text{ and}$$

$$1 < b^{-1} a_\nu < b; \text{ hence}$$

$$a_\nu < a_\nu b^{-1} a_\nu < a_\nu b \text{ and}$$

$$1 < a_\nu b^{-1} < (a_\nu b^{-1})^2 < a_\nu. \text{ Put } a_\nu b^{-1} = a_{\nu+1}, \text{ then}$$

(see 19) $0 < {}_a\lg a_{\nu+1} \leq \frac{1}{2}\,{}_a\lg a_\nu$. Hence one can construct a sequence of positive elements not belonging to E for which

$${}_a\lg a = 1,\ 0 < {}_a\lg a_2 \leq \tfrac{1}{2}, \ldots,\ 0 < {}_a\lg a_n \leq \tfrac{1}{2}\,{}_a\lg a_{n-1} \leq 2^{-n}, \ldots \qquad (20)$$

holds. For every **n** there exists integral numbers **r** and **s** such that

$$a_n{}^r \leq a < a_n{}^{r+1},\ a_n{}^s \leq \beta < a_n{}^{s+1}. \text{ Hence}$$

$$a_n{}^{r+s} \leq a\beta < a_n{}^{r+s+2}$$

$$a_n{}^{s-1} < a\beta a^{-1} < a_n{}^{s+2} \text{ and } a_n{}^{-2} < (a, \beta) < a_n{}^2$$

Thus $|(a, \beta)| < a_n{}^2 \leq a_{n-1}$ for $\mathbf{n} = 2, 3, \ldots$. Hence ${}_a\lg\,|(a, \beta)| = 0$ *i.e.*, $(a, \beta) = \epsilon$. Now $(a, \beta)^m = (a, \beta)\,(\beta, a^2)\,a^2\beta^2\,(a\beta)^{m-2} = \epsilon_1 a^2\beta^2\,(a\beta)^{m-2} = \ldots = \epsilon' a^m \beta^m$ for any positive **m**.

Moreover $a^u \leq a^m < a^{u+1}$, ${}_a\lg a = \operatorname{Lim}_{m\to+\infty} \mathbf{u} : \mathbf{m}$

$$a^v \leq \beta^m < a^{v+1},\ {}_a\lg\beta = \operatorname{Lim}_{m\to+\infty} \mathbf{v} : \mathbf{m}$$

$$a^{u+v-1} < \epsilon' a^m \beta^m = (a\beta)^m < a^{u+v-2},\ {}_a\lg(a\beta) = \operatorname{Lim}_{m\to+\infty} (\mathbf{u} + \mathbf{v}) : \mathbf{m}.$$

Hence ${}_a\lg(a\beta) = {}_a\lg a + {}_a\lg\beta$.

Thus (17) holds in every case.

The mapping $a \to {}_a\lg a$ is therefore a homomorphism mapping A on the modul of the real numbers ${}_a\lg a$ and E on 0. Thus this homomorphism is an isomorphism of A/E.

RAMAN EFFECT AND HYDROGEN BONDS

Part VII. Study of a Few Typical Carboxylic Acids

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In continuation of the study of the Raman spectra of acetic acid and its solutions in various solvents (Parts III, IV and V)[1] a few typical carboxylic acids have now been examined with a view to make the survey more comprehensive.

Propionic acid.—The Raman spectrum of this acid was investigated by a number of workers in the past.[2] They recorded only one broad line in the region of the C=O frequency. For our investigation pure dry propionic acid was prepared by redistillation of the acid kept over fused sodium propionate for a day. The following frequencies were obtained:—

290 (1) 480 (3) 610 (1) 846 (6) 1001 (3) 1080 (5) 1257 (2) 1420 (5) 1460 (4) 1668 (10*b*) 1710 (0) 1740 (0).

The two lines with (0) intensities were very distinct though very faint. They were not recorded by previous workers. Thus the spectrum of propionic acid bears a very close resemblance to that of acetic acid in the C=O region. The spectrum was quite unaffected in carbon tetrachloride solution. With a solution of the acid in water (1:1) the 1668 cm.$^{-1}$ line becomes almost extinct and the 1710 cm.$^{-1}$ line very intense; the 1740 cm.$^{-1}$ line was not recorded at all. A dioxan solution (1 : 1) gave the three lines with almost equal intensity due to the first having become weaker and the other two much stronger. If the proportion of acid to dioxan was 1 : 3, the first line vanished, the other two persisting. The 1740 cm.$^{-1}$ line was more intense than the 1710 cm.$^{-1}$ line. Thus the behaviour of these solutions is also parallel to that of acetic acid solutions. Consequently the mechanism of the changes is the same as described in the case of acetic acid, the three entities involved being (1) ring dimers, (2) open dimers and (3) monomers; (2) and (3) take part in complex formation with the solvents employed.

Formic acid.—This acid is known to differ from its homologues in a number of respects, the most important being its marked strength as an acid and its reducing properties. An explanation of these characteristics was given in a note to *Current Science*.[3] Hence it was felt necessary to study the Raman spectrum of pure formic acid and of its solutions in certain select solvents.

The Raman spectrum of formic acid has been studied by several workers in the past[4]; but the records are not entirely in agreement. The following gives the complete spectrum of a sample carefully purified by repeated distillation as obtained by us:—

190 ± 80 (8) 675 (3) 700 (1) 1048 (2) 1205 (2) 1400 (10) 1670 (8*b*) 1725 (4*b*) 2963 (7).

The broad and bright band at 190 cm.$^{-1}$ is remarkable since it is present only in the spectrum of formic acid and not in those of its homologues. It has been previously noted by Parthasarathy[5] and by Ganesan and Venkateswaran[6] but was not reported by Dadieu and Kohlrausch.[7] In the region of the C=O frequency Parthasarathy (*loc. cit.*) reported 1672 and 1724 cm.$^{-1}$ lines and Kohlrausch, Koppel and Pongratz[8] 1675 and 1728 cm.$^{-1}$ lines. But Koteswaram could get only a broad frequency at 1702 cm.$^{-1}$

An aqueous solution of formic acid was first studied by Parthasarathy. He noticed that the band at 189 cm.$^{-1}$ underwent a slight shift and narrowing. In the place of the two C=O lines of the pure acid he obtained a diffuse line with a maximum at 1697 cm.$^{-1}$ These changes were attributed to the formation of hydrates. Koteswaram observed a shift of the maximum of the broad line at 1702 cm.$^{-1}$ towards higher frequencies and attributed it to simple depolymerisation.

Mixtures of formic acid with various solvents have now been investigated. The significant results are given below:

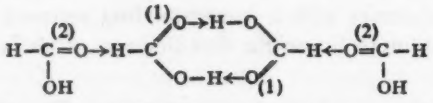
Water mixtures.—190 cm.$^{-1}$ band narrowed down, the 1670 cm.$^{-1}$ line decreased in intensity and the 1725 cm.$^{-1}$ line increased in intensity. In a solution having acid and water in the proportion 1 : 3, the 1670 cm.$^{-1}$ line became very faint though it did not disappear altogether.

Dioxan mixtures.—Formic acid and dioxan in the proportions 1 : 1 and 1 : 3 were employed. The 190 cm.$^{-1}$ band narrowed down; the 1670 cm.$^{-1}$ line decreased in intensity with a corresponding increase in the 1725 cm.$^{-1}$ line. In the more dilute solution the first line was more faint and the second much stronger.

Acetal, acetone and ethyl acetate mixtures.—The solutions in acetal behaved very similar to those in dioxan. In acetone solutions C=O frequencies could not be studied due to the existence of the strong C=O frequency of acetone falling in this region. But the narrowing of the band at 190 cm.$^{-1}$ was observed. The changes in ethyl acetate mixtures were again similar to those taking place in dioxan. But how far the C=O frequency of the ester (1740 cm.$^{-1}$) could have rendered the observation inexact could not be gauged. The narrowing down of the 190 cm.$^{-1}$ band is, however, significant in this case also.

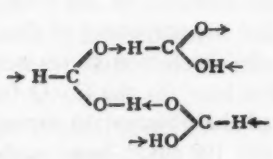
Discussion of results.—There is ample evidence for the existence of formic acid in the plolymeric form. The presence of ring dimers has been proved by the method using electron diffraction.[10] The changes taking place in mixtures with water and other kationoid and anionoid solvents may be expected to be somewhat similar to those found in the case of acetic and propionic acids. But there are obviously marked differences arising from the very nature of the formic acid molecule and the complications that it may give rise to. The chief item to be noted is the capacity of H of the CH in formic acid to form H bonds in addition to the OH of the carboxyl. This naturally introduces complications that have to be taken account of. The changes in 190 cm.$^{-1}$ band are in some manner connected with depolymerisation of formic acid aggregates and formation of heteromolecular associates. The smallness of the frequency shift appears to suggest that we are here concerned with a phenomenon involving aggregation only less in size compared with crystal aggregates. But the exact correlation is not clear.

The 1670 cm.$^{-1}$ line and the change it undergoes seem to be common to all the aliphatic acids. It is therefore right to attribute it to the C=O groups existing in ring dimers. Instead of the two lines of acetic and propionic acids (1710 and 1740 cm.$^{-1}$) which change markedly on admixture with other solvents, formic acid has only one broad line at 1725 cm.$^{-1}$ which is fairly strong even in the pure acid and brightens up in the mixtures. Obviously in the case of this acid no un-co-ordinated C=O is possible under any circumstances and the 1725 cm.$^{-1}$ line corresponds to a linearly co-ordinated C=O. This leads us to the inference that in the pure acid there is an appreciable proportion of C=O groups linearly co-ordinated and that this increases in the mixtures. The following tentative structures are suggested to exist in the pure acid (I, II) and in mixtures (others).

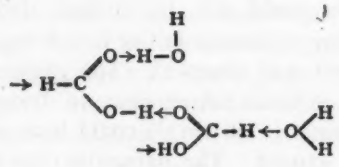


C=O (1) frequency 1670 cm.$^{-1}$ C=O (2) frequency 1725 cm.$^{-1}$

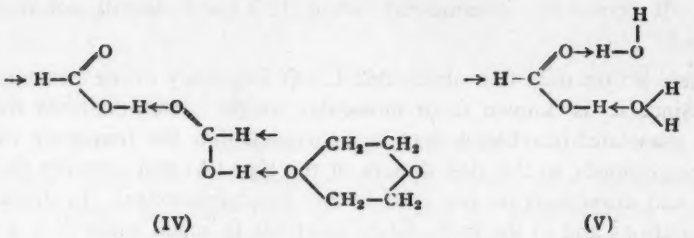
(I)



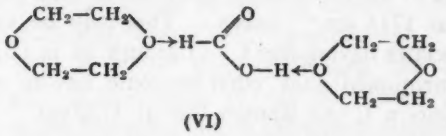
(II)



(III)

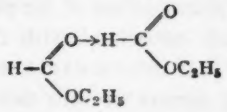


(IV) (V)



(VI)

In this connection may be mentioned a similar peculiarity noted with ethyl formate. Whereas ethyl actate and esters of other aliphatic acids have a sharp C=O frequency at 1740 cm.$^{-1}$, formates have a rather broad line at 1715 cm.$^{-1}$ The low value of this frequency and its breadth may be due to association of the ester molecules by means of hydrogen bonds. This point requires careful verification by other methods and is being studied.



Benzoic acid.—The Raman spectra of benzoic acid in solvents such as benzene, ether and alcohol were studied by Dadieu and Kohlrausch.[11] The C=O frequencies recorded were 1648, 1716 and 1689 cm.$^{-1}$ respectively. Koteswaram studied the molten substance and its solutions in benzene and water. He recorded 1654 cm.$^{-1}$ for the free acid and benzene solutions and 1728 cm.$^{-1}$ for the aqueous solutions at 100° C. Sunanada bai[12] has noted the C=O frequency of the molten acid as 1660 cm.$^{-1}$

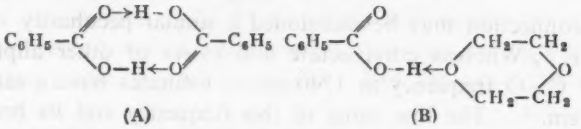
The following is the spectrum of the pure molten acid as observed by us:

160 (1) 172 (3) 422 (3) 480 (?) 625 (6) 648 (0) 800 (4) 820 (0) 999 (10) 1016 (2) 1030 (0) 1109 (1) 1176 (1) 1270 (3) 1560 (8) 1598 (4).

The C=O line remained practically unaffected in the benzene solution. On the other hand in ether this disappeared and a new C=O frequency was recorded at 1710 cm.$^{-1}$ and this was more prominent than the original line at 1650 cm.$^{-1}$ A solution in dioxan gave the same result, *i.e.*, new C=O line was at 1715 cm.$^{-1}$ and the original one at 1650 cm.$^{-1}$ was absent. In acetal solution (1:1) besides the 1715 line, the 1650 cm.$^{-1}$ line could be observed

faintly. It however disappeared when 1 : 3 (acid : acetal) solution was employed.

There is thus only one observable C=O frequency in the benzene solution. Since it is known from molecular weight determinations that the acid is associated (double) it may be concluded that the frequency of 1650 cm.$^{-1}$ corresponds to the ring dimers of the type (A) and possibly the open dimers and monomers do not exist to any detectable extent. In dioxan and ether solutions and in the more dilute solutions in acetal again only a bright C=O frequency at 1715 cm.$^{-1}$ exists. This may be said to correspond to monomer associates having free C=O groups as in (B). In justification of this may be mentioned that ethyl benzoate having an unco-ordinated C=O group exhibits a C=O Raman line at 1720 cm.$^{-1}$



(A) (B)

In less dilute solutions in acetal both lines appear though the 1650 cm.$^{-1}$ line is very feeble indicating that both types of molecules exist simultaneously. It is remarkable that there is no indication of the presence of the intermediate stage of open dimers and their associates with the solvents employed. It may be tentatively suggested that in this case they are unstable and either undergo change into the ring dimers or into monomer associates with the solvents. The breaking up of the dimers of the acid through H bond formation seems to be more easy than in the case of the aliphatic acids.

Cinnamic acid.—The behaviour of the unsaturated acid, cinnamic acid is very similar to that of benzoic acid. The following is the Raman Spectrum of the molten acid:—

153 (2*b*) 615 (1) 675 (0) 875 (2) 990 (1) 1002 (8) 1027 (3) 1077 (1) 1110 (1) 1181 (5) 1194 (6) 1260 (7) 1490 (2) 1598 (7) 1624 (10*b*) 1654 (2*b*).

Of the last 3 lines 1598 cm.$^{-1}$ frequency is attributed to the double bond of the benzene ring and 1624 cm.$^{-1}$ to the extra nuclear double bond. The last line, 1654 cm.$^{-1}$ is attributable to the C=O group of the acid. In benzene solution this line appeared at 1658 cm.$^{-1}$ and obviously represents ring dimers. No other line was noted in the C=O region. In dioxan solution this disppeared and a new line appeared at 1708 cm.$^{-1}$ thus indicating that complete break down into monomer associates with the solvent occurs. In support of the above contention may be stated (1) that cinnamic acid has double the molecular weight in benzene solution, (2) that the unco-ordinated C=O frequency should be at about 1708 since ethyl cinnamate has

the C=O line in this region and (3) the shift in the C=O Raman line due to formation of ring dimers (about 50 wave numbers) is according to expectation as judged from other cases. There is thus complete similarity between benzoic and cinnamic acids.

Summary and Conclusion

Raman spectra of (1) propionic acid, (2) formic acid, (3) benzoic acid and (4) cinnamic acid have been studied using the pure acids in the liquid or molten condition and solutions in various solvents, benzene (non-associating), water, ether dioxan, acetal, etc. (associating). The first closely resembles acetic acid both of them indicating the existence of ring dimers, open dimers and monomers, the last two forms being present to a very small extent in the free state and in increasing quantities (in association with solvents) in solution in associating liquids. The state of the molecules in formic acid seems to be more complex due probably to the capacity of H of the C–H group to form hydrogen bonds. There are 2 broad C=O lines equally strong in the pure liquid at 1670 and 1715 cm.$^{-1}$; the former diminishes and the latter increases in solutions with associating solvents. The narrowing of the band at 190 cm.$^{-1}$ is another characteristic. It seems to be possible that in this acid no molecular type having unco-ordinated C=O exists. Benzoic and cinnamic acids form a different type. The molten acids and benzene solutions give only one C=O line corresponding to ring dimers and in fairly dilute solutions in ethers monomer-associates alone containing unco-ordinated C=O groups exist. Thus they do not give indications of the intermediate open type of dimers.

REFERENCES

1. Murty and Seshadri, *Proc. Ind. Acad. Sci.*, A, 1942, **15**, 230, 238 ; **16**, 50.
2. *Vide* Bibliography given at the end of " Raman Effect and its Chemical Applications ", by James Hibben, Reinhold Publishing Corporation, New York, 1939.
3. Seshadri, *Curr. Sci.*, 1936, **4**, 651, 812.
4. *Vide* Ref. 2.
5. Parthasarathy, *Ind. J. Phys.*, 1931, **6**, 287.
6. Ganesan and Venkateswaran, *ibid.*, 1929, **4**, 196.
7. Dadieu and Kohlrausch, *Wien. Ber.*, 1930, **139**, 77 ; *Monatsh.*, 1930, **55**, 379.
8. Kohlrausch, Koppel and Pongratz, *Z. Physik. Chem.*, Abt. B, 1935, **21**, 615.
9. Koteswaram, *Z. Physik.*, 1939, **112**, 395.
10. Pauling and Brockway, *Proc. Nat. Acad. Sci.*, 1934, **20**, 336.
11. Dadieu and Kohlrausch, *Phys. Z.*, 1930, **31**, 514.
12. Sunandabai, *Proc. Ind. Acad. Sci.*, A, 1940, **11**, 216.

FORCE-CONSTANTS AND NORMAL MODES OF THE TOTALLY SYMMETRIC VIBRATIONS IN α-QUARTZ AT ROOM TEMPERATURE

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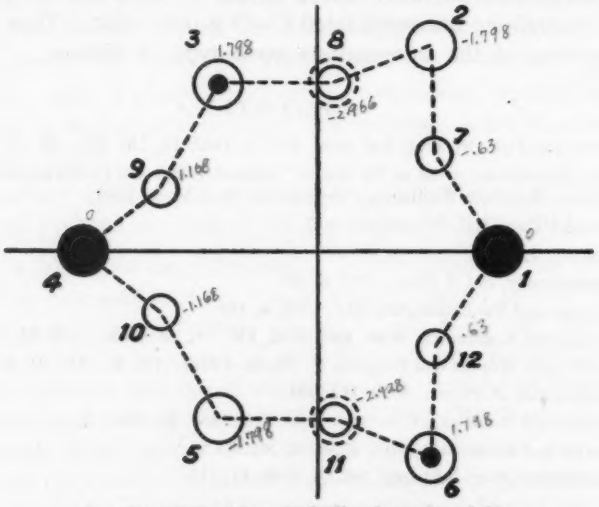
1. *Introduction*

In an earlier paper (author, 1940) it was shown that α-quartz possesses four totally symmetric vibrations, namely, 207, 356, 466 and 1082. In this paper the force-constants in α-quartz are derived by assuming these frequencies, and the normal modes of vibration of these frequencies have been obtained. The theoretical results are in complete agreement with the conclusions drawn in the above paper, regarding the nature of these lines, on the basis of the experimental results. The calculations have been made by adopting group-theoretical methods. The X-ray structure of α-quartz, the character table, and the symmetry modes of vibration have been discussed fully in the paper referred to above.

2. *Co-ordinates of* 12 *Atoms in α-Quartz*

The unit cell of α-quartz contains 3 silicon (1, 3, 5) atoms, and 6 oxygen atoms (7, 8, 9, 10, 11, 12). But as all equivalent points of the lattice have



○ are oxygen atoms vertically above 8 and 11

Their Z Co-ordinates are 2·428 for atom above 8 and 2·966 for atom above 11

the same motion at any given instant, the motions of silicon atoms 2, 4, 6, although exactly the same as those of 5, 1, 3, have to be taken into consideration in finding the potential and kinetic energy of the vibrations of the unit cell. The co-ordinates of 12 atoms (6 silicon and 6 oxygen atoms) for rectangular axes are:—

TABLE I

Atom No.	Atom type	x	y	z
−8	O	·3322	1·853	−2·966 or (2·428) for ○
2	Si	1·318	2·282	−1·798
7	O	1·4386	1·214	− ·630
1	Si	2·244	0	0
12	O	1·4386	−1·214	·630
6	Si	1·318	−2·282	1·798
11	O	·3322	−1·853	−2·428 or (2·966) for ○ oxygen atom
5	Si	−1·122	−1·944	−1·798
10	O	−1·7708	− ·6389	−1·168
4	Si	−2·635	0	0
9	O	−1·7708	·6389	1·168
3	Si	−1·122	1·944	1·798

The vertical distance between two consecutive oxygen and silicon atoms is taken as ·63 and 1·168 Å.U. Thus between two silicon atoms 3 and 4 there are two oxygen atoms 9 and 12 of which atom 9 is 1·168 Å above the silicon plane of (1, 4) atoms and atom 12 is 1·168 Å below the silicon plane of atoms (3, 6). With these co-ordinates we calculate the various distances and angles in α-quartz, and compare their values with those given by Bragg and Gibbs from X-ray evidence.

TABLE II

Distances, angles, etc.	Calculated value	Bragg and Gibbs' value
1. Si—O distance	1·588 Å	1·59 Å
2. Si—Si „	3·049 Å	3·05 Å
3. O—O „	2·735 Å 2·664 Å	2·72 Å 2·66 Å about
4. Angles made by the oxygen atoms at the silicon atom	114° 119°	
5. Angle made by two silicon atoms at the oxygen atom	147°·30′	147°
6. ∠345 = ∠561 = ∠123	104°−18′ = 120° − (15°−42′)	
∠451 = ∠612 = ∠432	135°−48′ = 120° + (15°−48′)	
7. Rotation about the c-axis of the triangle of the projected Si-atoms from the positions occupied by them in high quartz	$\frac{15°-45'}{2}$ = 7°·53′	About 8°
8. Distance from the origin of the projections of O-atoms on the basal plane	$\frac{1}{7}$·882 Å	

3. *Symmetry Co-ordinates*

The four frequencies belonging to the totally symmetric class are 207, 356, 466 and 1082. The symmetry co-ordinates for these have been shown to be

(i) $x_7+x_8+x_9+x_{10}+x_{11}+x_{12}$ (A)

(ii) $x_2+x_4+x_6$ (B)

(iii) $y_7+y_9+y_{11}-y_8-y_{10}-y_{12}$ (C)

(iv) $z_8+z_{10}+z_{12}-z_7-z_9-z_{11}$ (D)

As the silicon atom pairs (1, 4), (3, 6) and (2, 5) have the same motions at any instant, the second co-ordinate can be written as

$$x_2+x_4+x_6-x_1\ -x_3-x_5.$$

Each $+x_i$ is directed towards a point in the basal plane containing the given atom where the threefold axis meets it, z_i is perpendicular to the basal plane and positive upwards, y_i is at right angles to both and is positive in a direction making the motion right-handed. Let β, γ, δ, ϵ be the displacements of the atoms for the four symmetry modes A, B, C, D respectively. The co-ordinates of the displaced atoms are now

TABLE III

Atom	x	y	z
8—O	$\cdot3322-\frac{\cdot3322}{1\cdot882}\beta-\frac{1\cdot853}{1\cdot882}\delta$	$1\cdot853-\frac{1\cdot853}{1\cdot882}\beta+\frac{\cdot3322}{1\cdot882}\delta$	$-2\cdot966+\epsilon$
2—Si	$1\cdot318-\frac{\gamma}{2}$	$2\cdot282-\frac{\sqrt{3}}{2}\gamma$	$-1\cdot798$
7—O	$1\cdot4386-\frac{1\cdot4386}{1\cdot882}\beta+\frac{1\cdot214}{1\cdot882}\delta$	$1\cdot214-\frac{1\cdot214}{1\cdot882}\beta-\frac{1\cdot4386}{1\cdot882}\delta$	$-\cdot63-\epsilon$
1—Si	$2\cdot244+\gamma$	0	0
12—O	$1\cdot4386-\frac{1\cdot4386}{1\cdot882}\beta+\frac{1\cdot214}{1\cdot882}\delta$	$-\left(1\cdot214-\frac{1\cdot214}{1\cdot882}\beta-\frac{1\cdot4386}{1\cdot882}\delta\right)$	$\cdot63+\epsilon$
6—Si	$1\cdot318-\frac{\gamma}{2}$	$-\left(2\cdot282-\frac{\sqrt{3}}{2}\gamma\right)$	$1\cdot798$
11—O	$\cdot3322-\frac{\cdot3322}{1\cdot882}\beta-\frac{1\cdot853}{1\cdot882}\delta$	$-\left(1\cdot853-\frac{1\cdot853}{1\cdot882}\beta+\frac{\cdot3322}{1\cdot882}\delta\right)$	$-2\cdot428-\epsilon$
5—Si	$-\left(1\cdot122+\frac{\gamma}{2}\right)$	$-\left(1\cdot944+\frac{\sqrt{3}}{2}\gamma\right)$	$-1\cdot798$
10—O	$-\left(1\cdot7708-\frac{1\cdot7708}{1\cdot882}\beta-\frac{\cdot6389}{1\cdot882}\delta\right)$	$-\left(\cdot6389-\frac{\cdot6389}{1\cdot882}\beta+\frac{1\cdot7708}{1\cdot882}\delta\right)$	$-1\cdot168+\epsilon$
4—Si	$-(2\cdot635-\gamma)$	0	0
9—O	$-\left(1\cdot7708-\frac{1\cdot7708}{1\cdot882}\beta-\frac{\cdot6389}{1\cdot882}\delta\right)$	$\left(\cdot6389-\frac{\cdot6389}{1\cdot882}\beta+\frac{1\cdot7708}{1\cdot882}\delta\right)$	$1\cdot168-\epsilon$
3—Si	$-\left(1\cdot122+\frac{\gamma}{2}\right)$	$\left(1\cdot944+\frac{\sqrt{3}}{2}\gamma\right)$	$1\cdot798$

ERRATA

Page 271, line 2, *for* " have to be " *read* " should be "

„ „ 3, *for* " and Kinetic energy " *read* " and the kinetic energy "

„ Table I, under Atom No., *for* " –8 " *read* " 8 "

„ Table II, Serial No. 8, *for* " 1·882 Å " *read* " 1·882 Å "

Page 272, Table III, line 5 from the bottom, *for* " $\frac{\sqrt{3}}{2}$ " *read* " $\frac{\sqrt{3}}{2}\gamma$ "

Page 273, under section 4, lines 3 and 5, in place of " γ " substitute " r "

Page 275, line 10, *for* " 330 " *read* " 356 "

4. *Potential and Kinetic Energy*

The variations of the various Si—O distances and the variations of O\Si—O and O—Si/O angles can now be calculated.

$$\Delta\gamma_{2,8} = \Delta\gamma_{2,7} = \Delta\gamma_{6,12} = \Delta\gamma_{6,11} = \Delta\gamma_{4,10} = \Delta\gamma_{4,9}$$
$$= \frac{\cdot 5974\,\beta - \cdot 8644\,\gamma + \cdot 8946\,\delta - 1\cdot 168\,\epsilon}{1\cdot 588} = \Delta p$$

$$\Delta\gamma_{7,1} = \Delta\gamma_{1,12} = \Delta\gamma_{5,11} = \Delta\gamma_{5,10} = \Delta\gamma_{3,9} = \Delta\gamma_{3,8}$$
$$= \frac{-\cdot 1676\,\beta + \cdot 8054\,\gamma - 1\cdot 447\,\delta + \cdot 63\,\epsilon}{1\cdot 588} = \Delta q$$

$$\Delta\phi_{7,2,8} = \Delta\phi_{12,6,11} = \Delta\phi_{10,4,9}$$
$$= \frac{-2\cdot 546\,\beta + 2\cdot 431\,\gamma - \cdot 113\,\delta - 1\cdot 387\,\epsilon}{2\cdot 305} = (\Delta\chi_1)$$

$$\Delta\phi_{7,1,12} = \Delta\phi_{11,5,10} = \Delta\phi_{9,3,8}$$
$$= \frac{-2\cdot 634\,\beta - 2\cdot 391\,\gamma + \cdot 585\,\delta + \cdot 651\,\epsilon}{2\cdot 207} = (\Delta\chi_2)$$

$$\Delta\phi_{2,7,1} = \Delta\phi_{1,12,6} = \Delta\phi_{5,11,6} = \Delta\phi_{5,10,4} = \Delta\phi_{4,9,3} = \Delta\phi_{3,8,2}$$
$$= \frac{-\cdot 7914\,\beta - \cdot 4783\,\gamma + 1\cdot 018\,\delta + \cdot 9915\,\epsilon}{1\cdot 355} = (\Delta\chi_3)$$

If we assume k as Si—O force constant, k_1 as O—Si/O and k_2 as Si—O\Si deformation force constants the potential energy is given by

$$2\,V = 6\,k\,\{(\Delta p)^2 + (\Delta q)^2\} + 6\,k_1\,(\Delta\chi_3)^2 + 3\,k_2\,\{(\Delta\chi_1)^2 + (\Delta\chi_2)^2\}$$

which gives on expanding

$$6\,\{a\beta^2 + b\gamma^2 + c\delta^2 + d\epsilon^2 - 2\,e\beta\gamma + 2\,f\beta\delta - 2\,g\beta\epsilon - 2\,h\gamma\delta + 2\,i\gamma\epsilon - 2\,j\delta\epsilon\}$$

where

$$\begin{aligned}
a &= \cdot 1525\,k + \cdot 3412\,k_1 + 1\cdot 322\,k_2 \\
b &= \cdot 5535\,k + \cdot 1246\,k_1 + 1\cdot 143\,k_2 \\
c &= 1\cdot 1476\,k + \cdot 5641\,k_1 + \cdot 0363\,k_2 \\
d &= \cdot 6984\,k + \cdot 5356\,k_1 + \cdot 2247\,k_2 \\
e &= \cdot 2581\,k - \cdot 2061\,k_1 - \cdot 064\,k_2 \\
f &= \cdot 3080\,k - \cdot 4388\,k_1 - \cdot 1311\,k_2 \\
g &= \cdot 3184\,k + \cdot 4274\,k_1 - \cdot 1564\,k_2 \\
h &= \cdot 7687\,k + \cdot 2652\,k_1 + \cdot 1694\,k_2 \\
i &= \cdot 6015\,k - \cdot 2583\,k_1 - \cdot 4771\,k_2 \\
j &= \cdot 7757\,k - \cdot 5495\,k_1 - \cdot 0539\,k_2
\end{aligned}$$

The kinetic energy is given by

$$2\,T = 6\,m_1\dot{\beta}^2 + 6\,m_2\dot{\gamma}^2 + 6\,m_1\dot{\delta}^2 + 6\,m_1\dot{\epsilon}^2$$

where $m_1 = 16$ and $m_2 = 28{\cdot}3$.

The energy equation gives

$$\left.\begin{array}{lllll} (a-16\lambda^2)\beta & -e\gamma & +f\delta & -g\epsilon & =0 \\ -e\beta & +(b-28{\cdot}3\lambda^2)\gamma & -h\delta & +i\epsilon & =0 \\ f\beta & -h\gamma & +(c-16\lambda^2)\delta & -j\epsilon & =0 \\ -g\beta & +i\gamma & -j\delta & +(d-16\lambda^2)\epsilon & =0 \end{array}\right\} \quad (1)$$

where λ^2 is a constant. The values of λ^2 are the roots of the determinantal equation

$$\begin{vmatrix} (a-16\lambda^2) & -e & f & -g \\ -e & (b-28{\cdot}3\lambda^2) & -h & i \\ f & -h & (c-16\lambda^2) & -j \\ -g & i & -j & (d-16\lambda^2) \end{vmatrix} = 0 \quad (2)$$

If $\Delta_1, \Delta_2, \Delta_3, \Delta_4$ are the minors of 2, we get

$$(a-16\lambda^2)\,\Delta_1 + e\Delta_2 + f\Delta_3 + g\Delta_4 = 0.$$

The frequency $\bar{\omega}$ in cm.$^{-1}$ is given by $\bar{\omega} = \dfrac{\lambda}{2\pi c}\sqrt{\dfrac{10^{29}}{1{\cdot}65}}$ where c is the velocity of light. [The term $\sqrt{\dfrac{10^{29}}{1{\cdot}65}}$ arises because $\lambda^2 = \dfrac{k \times 10^5 \text{ dynes}}{m \times 1{\cdot}65 \times 10^{-24} \text{ grs.}} = \dfrac{k}{m} \times \dfrac{10^{29}}{1{\cdot}65}$, k being the force constant term and m the atomic weight.]

5. *Calculation of Force-Constants*

On expanding the determinant (2) we get

$$\left.\begin{array}{l} 115916{\cdot}8\,\lambda^8 - \lambda^6\,[16744{\cdot}8\,k + 10948{\cdot}7\,k_1 + 16150{\cdot}4\,k_2] \\ + \lambda^4\,[151{\cdot}2\,k^2 + 1473{\cdot}3\,kk_1 + 2268{\cdot}4\,kk_2 + 1125{\cdot}6\,k_1k_2 + 536{\cdot}3\,k_2^2] \\ - \lambda^2\,[72{\cdot}90\,kk_2^2 + {\cdot}857\,k^2k_1 + 16{\cdot}87\,k^2k_2 + 148{\cdot}1\,kk_1k_2 + 19{\cdot}15\,k_1k_2^2] \\ + [{\cdot}0591\,k^2k_1k_2 + {\cdot}4127\,k^2k_2^2 + 2{\cdot}898\,kk_1k_2^2 + {\cdot}01225\,kk_2^3] \end{array}\right\} = 0 \quad (3)$$

If the observed frequencies are the roots of the given equation it should be given by

$$\lambda^8 - {\cdot}9122\,\lambda^6 + {\cdot}1698\,\lambda^4 - {\cdot}010177\,\lambda^2 + {\cdot}0001625 = 0. \quad (4)$$

Comparing the two equations (3) and (4) we find that k should lie between 5·0 and 5·1 and a good fit is obtained for

$$k = 5{\cdot}065 \times 10^5,\ k_2 = {\cdot}9491 \times 10^5,\ k_1 = {\cdot}5116 \times 10^5 \text{ dynes.}$$

These values are obtained by trial. The coefficients of λ^6 and λ^4 give two equations which enable us to eliminate k_1 and obtain an equation in k and k_2. Substituting for k we get a quadratic in k_2. These values of k and k_2 give k_1. The comparison of equations (3) and (4) gives four relations. We are thus able to satisfy four relations with the help of three constants only. By substituting the above values of k, k_1 and k_2 in equation (3) we get

$$\lambda^8 - \cdot 9122\,\lambda^6 + \cdot 1694\,\lambda^4 - \cdot 00973\,\lambda^2 + \cdot 0001474 = 0.$$

It gives the following values of frequencies in cm.$^{-1}$

$\bar{\omega}$ (calc.)	..	1082	483	336	201
$\bar{\omega}$ (obs.)	..	1082	466	356	207

If we substitute the above values of k, k_1 and k_2 in the determinantal equation (2) it becomes

$$\begin{vmatrix} (2\cdot 201 - 16\,\lambda^2) & -1\cdot 141 & 1\cdot 212 & -1\cdot 6835 \\ -1\cdot 141 & (3\cdot 952 - 28\cdot 3\,\lambda^2) & -4\cdot 19 & 2\cdot 463 \\ 1\cdot 212 & -4\cdot 190 & (6\cdot 135 - 16\,\lambda^2) & -3\cdot 597 \\ -1\cdot 6835 & 2\cdot 463 & -3\cdot 597 & (4\cdot 025 - 16\,\lambda^2) \end{vmatrix} = 0 \quad (6)$$

This on expansion becomes

$$115916\cdot 8\,\lambda^8 - 105740\cdot 3\,\lambda^6 + 19624\cdot 9\,\lambda^4 - 1128\cdot 49\,\lambda^2 + 17\cdot 6806 = 0 \quad (7)$$

which is equivalent to

$$\lambda^8 - \cdot 9122\,\lambda^6 + \cdot 1693\,\lambda^4 - \cdot 009735\,\lambda^2 + \cdot 0001525 = 0. \quad (8)$$

Equation (8) gives the following frequencies in cm.$^{-1}$

$\bar{\omega}$ (calc.)	..	1082	484	330	208
$\bar{\omega}$ (obs.)	..	1082	466	356	207

The agreement of the observed and calculated frequencies is fairly close and justifies the constants chosen.

6. *Normal Modes of Vibration*

The normal modes of vibration are merely linear combinations of the four symmetry modes A, B, C and D.

$$\mathrm{A} = x_7 + x_8 + x_9 + x_{10} + x_{11} + x_{12}$$
$$\mathrm{B} = x_2 + x_4 + x_6 - x_1 - x_3 - x_5$$
$$\mathrm{C} = y_7 + y_9 + y_{11} - y_8 - y_{10} - y_{12}$$
$$\mathrm{D} = z_8 + z_{10} + z_{12} - z_7 - z_9 - z_{11}$$

If β, γ, δ, ϵ be the displacements in the four modes A, B, C, D respectively, then since the mode B refers to silicon atoms of mass m_2 and modes A, C, D to oxygen atoms of mass m_1, the four normal modes are given by

$$\beta_i\,\mathrm{A} + \frac{m_2^{\frac{1}{2}}}{m_1^{\frac{1}{2}}}\,\gamma_i\,\mathrm{B} + \delta_i\,\mathrm{C} + \epsilon_i\,\mathrm{D};\ i = 1, 2, 3, 4. \quad (9)$$

As the normal modes are orthogonal to each other they must satisfy relations of the type

$$\beta_1\beta_2+\frac{m_2}{m_1}\gamma_1\gamma_2+\delta_1\delta_2+\epsilon_1\epsilon_2=0, \tag{10}$$

where $m_2=28\cdot3$ and $m_1=16$.

7. *Calculation of Coefficients β_i, etc.*

If Δ_1, Δ_2, Δ_3, Δ_4 are minors of determinant 2, the last three equations of (1) give

$$\frac{\beta}{\Delta_1}=\frac{-\gamma}{\Delta_2}=\frac{\delta}{\Delta_3}=\frac{-\epsilon}{\Delta_4}.$$

The normal mode (9) can now be written as

$$\Delta_1 A-\frac{m_2^{\frac{1}{2}}}{m_1^{\frac{1}{2}}}\ \Delta_2 B+\Delta_3 C-\Delta_4 D. \tag{11}$$

The values of minors Δ_1, Δ_2, Δ_3, Δ_4 for $k=5\cdot065\times10^5$, $k_1=\cdot5116\times10^5$ and $k_2=\cdot9491\times10^5$ dynes can easily be calculated from determinantal equation (6). We get

$$\left.\begin{aligned}
\Delta_1&=-7244\cdot8\,\lambda^6+5612\cdot1\,\lambda^4-597\cdot1\ \lambda^2+12\cdot817\\
\Delta_2&=\quad\ -292\cdot1\,\lambda^4+\ 37\cdot89\,\lambda^2-\ 3\cdot644\\
\Delta_3&=\quad\ -548\cdot8\,\lambda^4-\ 33\cdot17\,\lambda^2+\ 3\cdot765\\
\Delta_4&=\quad\ -762\cdot3\,\lambda^4+230\cdot4\ \lambda^2-\ 6\cdot496
\end{aligned}\right\} \tag{12}$$

The values of Δ_1, $\left(\frac{m_2}{m_1}\right)^{\frac{1}{2}}\Delta_2$, Δ_3 and Δ_4 for the various frequencies are given in Table IV.

TABLE IV

Observed frequency in cm.$^{-1}$	Calculated frequency in cm.$^{-1}$	Value of λ^2 for calculated value	Δ_1	$-\frac{m_2^{\frac{1}{2}}}{m_1^{\frac{1}{2}}}\Delta_2$	Δ_3	$-\Delta_4$
207	208	·02537	1·161	3·818	2·571	1·139
356	330	·06357	− 4·315	3·214	− ·569	− 5·072
466	484	·1377	18·11	5·273	− 11·20	− 10·784
1082	1082	·6853	−92·48	152·9	−276·7	206·6

8. *Discussion*

The normal modes for the four frequencies are:—

$$\begin{aligned}
1\cdot161\,A+3\cdot818\,B+2\cdot571\,C+1\cdot139\,D &\text{ for } \bar{\omega}=208\\
-4\cdot315\,A+3\cdot214\,B-\cdot569\,C-5\cdot072\,D &\text{ for } \bar{\omega}=330\\
18\cdot11\,A+5\cdot273\,B-11\cdot20\,C-10\cdot784\,D &\text{ for } \bar{\omega}=484\\
-92\cdot48\,A+152\cdot9\,B-276\cdot7\,C+206\cdot6\,D &\text{ for } \bar{\omega}=1082,
\end{aligned}$$

where A, B, C, D are the four symmetry modes. On the basis of the experimental results the author had associated the frequencies 207, 356, 466 and 1082 to symmetry modes B, D, A and C respectively. The theoretical results obtained here are in complete agreement with this conclusion. The greatest amplitudes for the above frequencies namely 3·818 for 208, 5·072 for 330, 18·11 for 484 and 276·7 for 1082 occur in the modes B, D, A and C respectively. The above results also give us an idea about the relative intensities of the various lines, although an exact calculation is not attempted here. It is easy to see that for the modes C and D the change of polarisability will be small while it will be relatively large for modes A and B. In fact if all the atoms were in one plane, the modes C and D would be forbidden in the Raman effect. We may assume that the intensity is proportional to the square of the electric moment M and that the changes in M are proportional to the amplitudes of vibration. Table IV shows that the amplitudes for modes A and B are much smaller than those in D for the line 1082, are comparable to those in D for the line 330, are greater than those in D for the lines 208 and 484. We may thus account for a very feeble intensity of the line 1082, for a comparatively greater intensity in 356, and for large intensities in 208 and 484. Further, as the mode B will show lesser change of polarisability than A, the line 208 will be weaker than 484.

In conclusion, I have to thank Professor Sir C. V. Raman for kindly suggesting the problem, and for other helpful discussions.

9. *Summary*

The force constants for α-quartz have been calculated with the help of the four frequencies of vibration 207, 356, 466 and 1082 belonging to the totally symmetric class. If we assume $k = 5{\cdot}065 \times 10^5$, $k_1 = {\cdot}5116 \times 10^5$, $k_2 = {\cdot}9491 \times 10^5$ dynes the frequencies calculated are 1082, 484, 330, 208 as against 1082, 466, 356, 207 observed. The agreement of calculated and observed frequencies is fairly close and justifies the force constants chosen. The normal modes of the calculated frequencies have also been obtained. The normal modes of different frequencies are:—

$$1{\cdot}161\,A + 3{\cdot}818\,B + 2{\cdot}571\,C + 1{\cdot}139\,D \text{ for } \bar{\omega} = 208$$
$$-4{\cdot}315\,A + 3{\cdot}214\,B - {\cdot}569\,C - 5{\cdot}072\,D \text{ for } \bar{\omega} = 330$$
$$18{\cdot}11\,A + 5{\cdot}273\,B - 11{\cdot}20\,C - 10{\cdot}784\,D \text{ for } \bar{\omega} = 484$$
$$-92{\cdot}48\,A + 152{\cdot}9\,B - 276{\cdot}7\,C + 206{\cdot}6\,D \text{ for } \omega = 1082$$

where A, B, C and D are the four symmetry modes discussed in a previous paper (author, 1940).

REFERENCES

Saksena, B. D. .. *Proc. Ind. Acad. Sci.*, A, 1940, **12**, 93.

Bragg and Gibbs .. *Proc. Roy. Soc. Lond.*, 1925, **109**, 425.

SCATTERING OF LIGHT IN BINARY LIQUID MIXTURES

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1. Introduction

In a paper published in these *Proceedings*, Sir C. V. Raman (1941) described a new technique for the study of light scattering which opens up an extensive vista of research both in molecular and in colloid optics. A nicol capable of rotation about its axis polarizes the beam of light which traverses through the diffusing medium while the transversely scattered light is observed through a Babinet compensator and a second nicol, the compensator fringes being viewed in focus through an eyepiece. The visibility and situation of these fringes is found to vary with the plane of polarization of the incident beam in a manner depending on the size as well as on the optical anisotropy of the particles scattering the light. In the present investigation, this technique is applied to the study of the scattering of light by binary liquid mixtures above the critical solution temperature where they exhibit a marked opalescence. The optical behaviour of such mixtures has engaged the attention of many investigators, including especially R. S. Krishnan (1935, 1937) who measured the depolarisation of the scattered light for various states of polarisation of the incident light and from his observations concluded that molecular clusters of appreciable size exist in several binary liquid mixtures in the vicinity of the critical solution temperature. The use of the Babinet compensator in the study of the opalescence of binary mixtures is of special value as it readily demonstrates the reality of the Krishnan effect reversal of polarisation and by revealing the existence of an elliptic polarisation in the diffused light—a phenomenon very evident in the case of ordinary emulsions (Darbara Singh, 1942)—also Krishnan's conclusions regarding the existence of clusters of appreciable dimensions. The complications which arise from repeated (secondary and tertiary) scattering of light, *viz.*, Rousset, (1934) and D. Venkateswara Rao (1942), are avoided in the present research by working at temperatures several degrees higher than the critical solution point.

2. Experimental Arrangements

Three binary liquid mixtures, *viz.*, phenol-water, carbon disulphide-methyl alcohol and methyl alcohol-normal hexane, have been studied, each at two different temperatures, one a few degrees above the critical temperature and the other considerably higher. In studying such mixtures, it is necessary to obtain them pure dust-free and with the correct critical composition as opalescence is then most pronounced. A small pyrex glass cross of capacity about 50 c.c. with arms of length one inch and diameter three quarters of an inch was employed as the container. This was joined to a pyrex glass bulb of slightly larger capacity by a narrow tube connected to the cross at the intersection of its two arms. The component liquids were taken from freshly opened bottles, purified by distillation, mixed in the correct critical proportion and poured into the glass bulb. The bulb and the cross were then immersed in freezing mixture, evacuated and sealed. The presence of dust particles could be detected by focussing a beam of sunlight by means of powerful lens and placing the cross in its path. They were eliminated by repeated slow distillation, the mixture being washed back into the bulb every time. The final distillation was carried out very slowly and the mixture was completely distilled over into the cross which was then sealed off. The cross was then placed within a copper vessel having three windows of strain-free pyrex glass plate, one for the entry of light, one for egress and the third for observation. The vessel was electrically heated by using a resistance of nichrome wire. The cross was kept immersed in dust-free water and could be maintained at any required temperature.

Sunlight was reflected into a dark cabin by means of a Foucault single-mirror heliostat and focussed on the cross by a Dallmeyer lens of variable aperture. The heat rays were cut off by placing a cell of alum solution close to the lens. A nicol provided with a graduated circle could polarise the incident light in any azimuth. A Babinet compensator with its principal plane inclined at 45° to the plane of observation was placed in the path of the transversely scattered light and next to it was mounted another nicol oriented so as to transmit vibrations with the electric vector horizontal. The compensator fringes could be viewed through an eye piece. For photographing them, the eye piece was removed and replaced by a camera.

In the ordinary Babinet compensator, two rectangular wedges of quartz are placed in contact, so that together they form a parallel plate of which the thickness can be altered by sliding the prisms along the interface. The compensator used in the present investigation was one in which the prisms could not be made to slide against each other but had instead a fixed wire

as a fiduciary mark inserted between the wedges. When plane polarised light is incident on the compensator parallel to the prismatic edges, the phase difference between the emergent rays will be equal to a whole number of wave-lengths along certain lines. There will, therefore, be equidistant lines of plane polarised light in the emergent light, which can be made to appear as dark bands by the use of the analysing nicol crossed with reference to the plane of polarisation of the light incident on the compensator. If, however the plane of vibration of the light incident on the compensator be parallel to that transmitted by the analysing nicol, the fringes appear in a displaced position, the cross-wire appearing on a bright band instead of on a dark one as when the two planes are crossed. The presence of ellipticity gives rise to a system of fringes of which the position with respect to the fixed cross wire depends upon the ellipticity.

3. Results

When the polarising nicol is so oriented as to transmit vertical vibrations, the field of vision is very bright and the fringes are very distinct, the cross-wire being at the centre of a dark band. As the nicol is slowly rotated, the fringes begin to lose intensity and at a particular setting depending on the liquid mixture are scarcely visible. Meanwhile, beginning from a particular orientation of the polarising nicol with respect to the horizontal position, the cross-wire begins to shift from the dark band, the shift increasing with diminishing inclination to the horizontal position until finally the cross-wire is at the centre of a bright band. This gradual shift of the fringes with respect to the cross-wire from dark to bright is an indication of ellipticity. On further rotation, the phenomena repeat themselves, the fringes becoming very bright once again when the incident vibrations are vertical. In the case of the two strongly scattering mixtures (phenol-water and carbon disulphide-methyl alcohol) all these phenomena could be visually observed. But for the methyl alcohol-normal hexane mixture, the scattering was rather feeble and hence visual observation was rather difficult. Photographs of the phenomenon were therefore taken for all the three mixtures for a series of positions of the polarising nicol at intervals of 2°. The phase difference corresponding to each setting has been evaluated from the shift of the fringes with respect to the cross-wire measured on the photographic plate by a micrometer reading up to 1/100 of a mm. Two typical sets of photographs are reproduced in Plate X. The following table gives the values of the phase differences for the various mixtures for a series of orientations of the polarising nicol.

TABLE I

θ measured from the horizontal position of the polarising nicol	Phase differences calculated in terms of π		
	Phenol-water (74° C.)	Carbon disulphide-methyl alcohol (45° C.)	Methyl alcohol-normal hexane (34° C.)
12°	0	0	0
10	·22	·12	·24
8	·44	·32	·53
6	·71	·60	·78
4	·89	·86	·95
2	1·0	1·0	1·0
0	1·0	1·0	1·0

These values when plotted exhibit the variation of the ellipticity with the plane of polarisation of the incident beam. It will be noticed that the curves resemble one another fairly closely. The temperature of measurement is in each case 5° above the critical solution temperature. The absolute intensity of the scattering is then sufficiently small to make the effects of secondary scattering which is so predominant at the critical temperature, quite negligible.

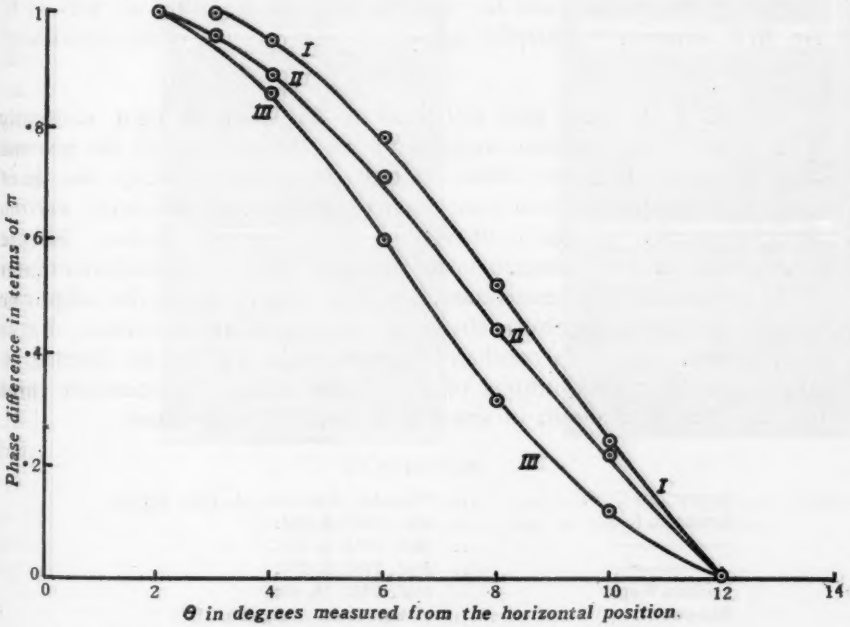


Fig 1. Ellipticity as a function of the plane of polarisation of the primary beam
I—Methyl alcohol–Normal hexane mixture 34° C.
II—Phenol–water mixture 74° C,
III—Carbon disulphide–methyl alcohol mixture 45° C.

The experiments were repeated in each case at 20° above the critical temperature and no trace of ellipticity could then be observed in any of the mixtures. The Krishnan effect, however continued to be observable, the fringes shifting more or less suddenly from one position to the other at the point of minimum visibility.

4. Discussion of the Results

The present investigation demonstrates the value of the new technique for the study of light scattering in which the Babinet compensator is employed for the detection of ellipticity as well as of a reversal of polarisation. Secondly, the results confirm Krishnan's conclusion regarding the formation of molecular clusters in liquid mixtures at and near the critical solution point, since, according to Mie's theory, for large spherical particles, ellipticity should be observed in all cases except when the incident light is vertically or horizontally polarised. Again, the absence of ellipticity at temperatures far removed from the critical solution temperature shows that the size of the clusters diminishes as one goes far away from the critical temperature. This is in good agreement with Krishnan's observations of the depolarisation factors.

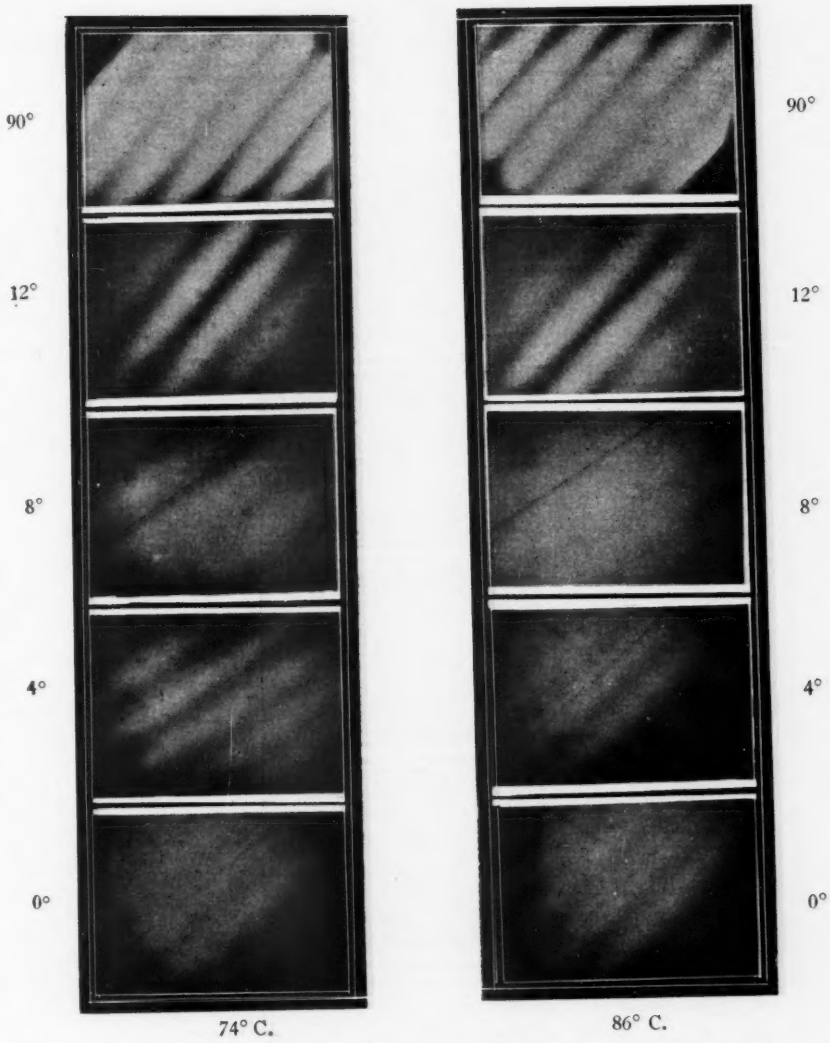
The author's grateful thanks are due to Prof. Sir C. V. Raman for suggesting the problem and for valuable help and guidance as well as to Dr. R. S. Krishnan for helpful suggestions in the course of the experiment.

5. Summary

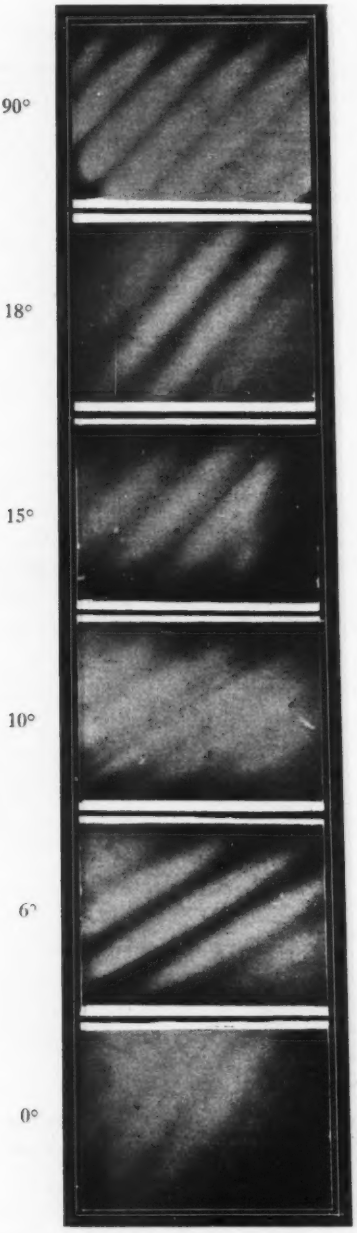
Sir C. V. Raman's new technique in the study of light scattering making use of the Babinet compensator for the detection of the reversal of polarisation (Krishnan effect) as well as of the ellipticity has been successfully applied to three binary liquid mixtures, phenol-water, carbon disulphide-methyl alcohol and methyl alcohol-normal hexane. Elliptic polarisation has been detected in the scattered light in the neighbourhood of the critical solution temperature. At higher temperatures, the ellipticity vanishes indicating thereby a change in the size of the particles. From these observations, it is concluded that molecular clusters are formed in mixtures in the neighbourhood of the critical solution temperature and that the clusters diminish in size with increase of temperature.

REFERENCES

Raman, Sir C. V. .. *Proc. Ind. Acad. Sci.*, A, 1941, **14**, 228.
Krishnan, R. S. .. *Ibid.*, 1935, **1**, 915.
——— .. *Ibid.*, 1935, **2**, 221.
——— .. *Ibid.*, 1937, **5**, 577.
Darbara Singh .. *Ibid.*, 1942, **15**, 406.
Rousset, A. .. *Compt. Rend.*, 1934, **198**, 2152.
Venkateswara Rao, D. .. *Proc. Ind. Acad. Sci.*, A, 1942, **15**, 24.



Light scattering in phenol-water mixture observed through a Babinet's compensator
(The angles are measured from the horizontal position)



Light scattering in silver sol VI observed through a Babinet's compensator
(The angles are measured from the horizontal position)

ELLIPTIC POLARISATION OF LIGHT SCATTERED IN SILVER SOLS

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Received September 8, 1942

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

The colours exhibited by metals in the colloidal state have interested physicists as well as colloid chemists for a very long time. While some of them tried to correlate the size of the colloidal particles with the colours exhibited by them, others maintained that it is the shape more than the size that influences colour. The latter view was particularly supported by Gans, who, from an estimation of absorption coefficients as well as the depolarisation factor ρ_h concluded that colloidal silver consists of particles that are prolate ellipsoids in shape with the axial ratio slightly less than unity. A detailed study of the dispersion of depolarisation as well as the extinction coefficient of a series of silver sols for wavelengths ranging from 2500 Å.U. to 7000 Å.U. has been made by Krishnan (1937). From his measurements, Krishnan concluded that the nuclear sol contains particles of extremely small size, whereas the sols prepared by using formalin as reducing agent and that obtained by the use of gold nuclear sol contain particles of size comparable with the wavelength of light. In the other sols Krishnan found particles of intermediate sizes. In view of the importance of the determination of the size and shape of colloidal particles and the bearing they have on the other physical properties of colloids, it was thought desirable to apply the new technique for the study of light scattering developed by Sir C. V. Raman (1941) to the case of silver sols.

2. Experimental Arrangements

A series of five unprotected silver sols have been chosen for the present investigation, the sols being representative of particular sizes of silver in the colloidal state. The sols were prepared by the methods given by Krishnan (1937) and preserved in thoroughly cleaned and well-steamed resistance glass bottles. The optical arrangements were the same as those described by the author in an earlier paper appearing in this same issue of the *Proceedings* with the difference that weather conditions necessitated the

use of a powerful carbon arc in place of sunlight. The sol was contained in a rectangular glass cell covered all over, top, bottom and the sides with black paper leaving only three windows for the entrance of light, for its exit and for observation. The arrangement of the Babinet compensator and the analysing nicol have all been described in the previous paper.

3. Experimental Observations

Nuclear Sol.—Conventionally known as Sol II, this is slightly yellowish in colour and the scattering is fairly intense. Visual observations could therefore be made by means of the eye piece attached to the compensator. When the incident light is polarised with vibrations vertical the system of fringes is very bright, the cross-wire being on a dark band and hardly distinguishable from it. As the polarising nicol is rotated the fringes gradually lose in intensity until they become almost invisible in the horizontal position. Even in this position, the cross-wire could be seen on the dark band itself, showing thereby that there is no reversal of polarisation. On further rotation, the fringes gain in intensity until they attain maximum brightness for vertical vibrations. Thus, in this sol neither reversal of polarisation nor ellipticity could be observed.

Sol III.—This is obtained by hydrogen peroxide reduction and is a clear sol containing bluish particles. When the incident light has its vibrations inclined at 12° to the horizontal, the fringes begin to shift with respect to the cross-wire and on further rotation of the polarising nicol go on shifting until in the horizontal position the cross-wire appears in the middle of a bright band. On still further rotation, the phenomenon repeats itself and the fringes continue to increase in intensity until they are brightest in the vertical vibration position of the polarising nicol.

Sol IV.—Obtained by formalin reduction, this is a bright yellow sol with fairly intense scattering. In this case, the phenomena are qualitatively the same as those for sol III, but the ellipticity is shown to a larger extent, extending to 16° on either side of the horizontal vibration direction.

Sol V—is prepared according to the method suggested by Voigt and Heumann for the preparation of uniform sols with particles of the same size and colour. Light yellow in colour, this shows elliptic polarisation to the same extent as sol III, but with slight differences in the degree of ellipticity for various settings of the polarising nicol.

Sol VI.—This is a yellowish brown sol formed by the use of gold nuclear sol and reduced by hydrogen peroxide. Of all the sols this shows the largest degree of ellipticity extending up to 18° on either side of the direction of horizontal vibration. Photographs of the compensator fringes

for different orientations of the polarising nicol obtained with sol VI are reproduced as Fig. 1 in Plate XI.

The degrees of ellipticity for the different sols are tabulated below and the graphs of ellipticity are given in the accompanying figure.

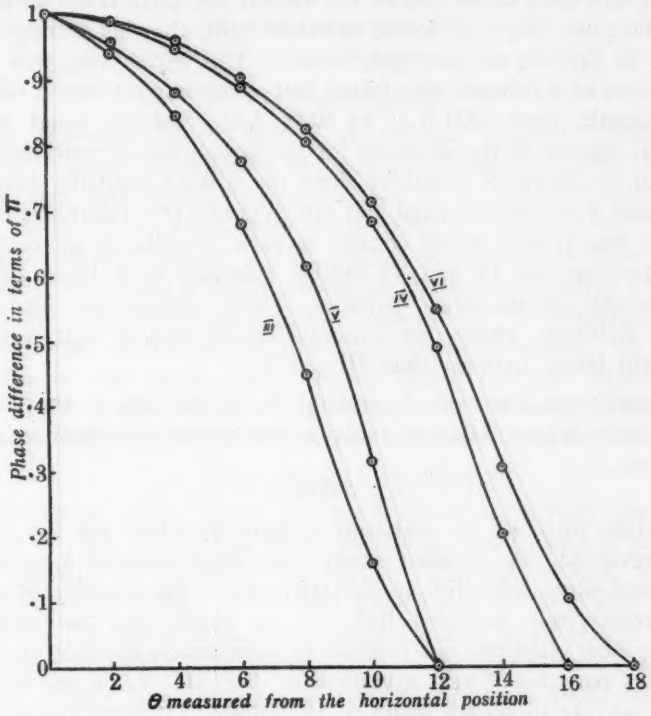

Fig. 1. Graph of ellipticity as a function of the plane of polarisation of the incident beam

TABLE I

θ measured from the horizontal position	Phase differences in terms of π			
	Sol III	Sol IV	Sol V	Sol VI
0	1	1	1	1
2	·94	·99	·96	·99
4	·84	·95	·86	·96
6	·68	·89	·77	·91
8	·45	·80	·62	·83
10	·16	·63	·31	·67
12	0	·49	0	·55
14	0	·20	0	·31
16	0	0	0	·1
18	0	0	0	0

4. Discusson of Results

According to the theory of Mie, in directions other than those parallel and perpendicular to the incident electric vector, the light scattered by large spherical particles would be elliptically polarised. The present investigation reveals that, in the case of the nuclear sol, there is neither reversal of polarisation nor ellipticity in the scattered light, showing thereby that the particles in this sol are extremely small. This agrees very well with the observations of Krishnan, who found that ρ_λ for this sol over a wide range of wavelengths from 3000 Å.U. to 6000 Å.U. remains equal to unity. Again the degrees of the ellipticity for the various sols as represented in the table and the curves of ellipticity show the striking similarity between the sols III and V on the one hand and sols IV and VI on the other, indicating that the two groups should contain in each particles of almost identical size. Moreover sols IV and VI exhibit ellipticity to a larger extent and hence should contain larger particles. These observations also support those of Krishnan whose depolarisation factors showed that sols IV and VI contain larger particles than III and V.

In conclusion, the author's grateful thanks are due to Prof. Sir C. V. Raman under whose inspiring guidance the present investigation has been carried out.

5. Summary

Previous work on the scattering of light by silver sols has been very briefly reviewed. A detailed study has been made of a series of five unprotected silver sols, with special reference to the presence of ellipticity in the transversely scattered light. It is found that the nuclear sol exhibits neither ellipticity nor reversal of polarisation showing thereby that it contains particles of very minute size. Sols III, V, IV and VI exhibit ellipticity in the increasing order of magnitude. It is concluded that the particles in IV and VI are larger than those in III or V. These results are in agreement with those obtained by Krishnan from a study of the dispersion of depolarisation as well as the extinction coefficients.

REFERENCES

Gans .. *Ann. d. Phys.*, 1915, **47**, 270 ; 1921, **62**, 331.
Raman, Sir C. V. .. *Proc. Ind. Acad. Sci.*, A, 1941, **14**, 228.
Krishnan, R. S. .. *Ibid.*, 1937, **5**, 305.
Hariharan, P. S. .. *Ibid.*, 1942, **16** (This issue).

THE RAMAN SPECTRUM OF SULPHUR UNDER HIGH DISPERSION

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1. *Introduction*

A large and clear natural crystal of rhombic sulphur having become available, it appeared desirable to study its Raman spectrum in order to confirm and supplement the observations of the author described in an earlier paper (1941) which were made with a comparatively small and artificially prepared crystal. In the present research, two different instruments were employed, a Hilger two-prism spectrograph giving a dispersion of 68 Å per mm. in the region of the green line of the mercury arc, and a Hilger Littrow prismatic spectrograph giving a dispersion of 26 Å per millimetre in the same region. It was hoped that the higher resolving power of the latter instrument might result in revealing some hitherto unrecorded features of the spectrum, and this anticipation has been realised.

2. *Experimental Arrangements*

The crystal was so placed that the *c*-axis of the crystal was along the direction of observation, this being horizontal and transverse to the light of the mercury arc traversing the crystal. The light entered the crystal normal to the (111) face. The study was carried out first with the instrument giving the smaller dispersion, as this required much smaller exposures. Condensing the light of the mercury arc on the crystal by a lens of large aperture, a good spectrogram could be obtained in about three hours. Careful examination of several spectrograms obtained with different exposures and with different slit-widths failed to reveal any new lines other than those already reported in the author's earlier paper. Some of the weaker lines, however, are more clearly recorded in the present studies.

The experiments were then repeated with the spectrograph having greater dispersion and resolving power. As the light-gathering power of this instrument is not very high, it required much longer exposures to get good spectrograms. The work, however, proved to be worthwhile as the spectrograms obtained showed the line-width and structure to vary greatly for the different frequency shifts. Using an iron arc spectrum as comparison, the line-widths could be measured and recorded. Typical spectra obtained with the two instruments enlarged so as to match each other are reproduced as Figs. 1 (*a*) and (*b*) in Plate XII.

3. *Results*

TABLE I. *Raman Spectra of Sulphur*

No.	Littrow Spectrograph		Two-Prism Spectrograph	
	Wave-number in cm.$^{-1}$	Relative Intensity	Wave-number	Relative Intensity
1 (*a*)	43–45	(8)	49	(8)
(*b*)	46–55	(10)		
2	76–90	(6)	84	(6)
3	108–112	(4)	114	($\frac{1}{2}$)
4	145–157	(10)	153	(10)
5	183	(2)	183	(2)
6	211–217	(8)	216	(10)
7	245	(1)	244	(2)
8	433	(3)	434	(3)
9	469–474	(7)	470	(9)

The most striking feature is the great width of the two Raman lines recorded with frequency shifts 50 and 85 respectively, indicating that these lines are really due to the superposition of several distinct frequencies. Indeed, in the spectrogram obtained with the Littrow instrument, the first line appears more or less clearly resolved into two components, the lower

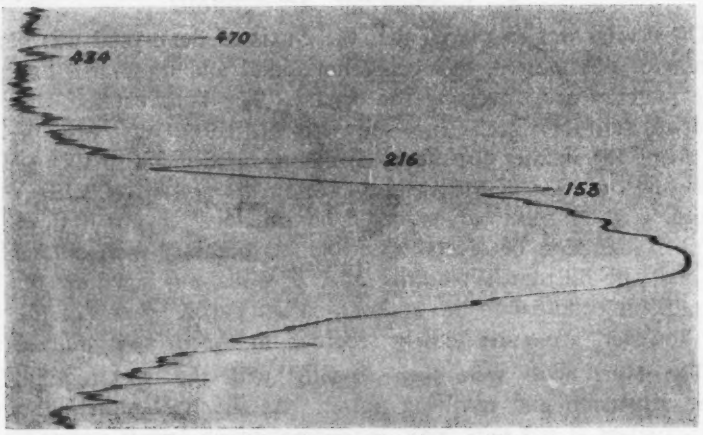
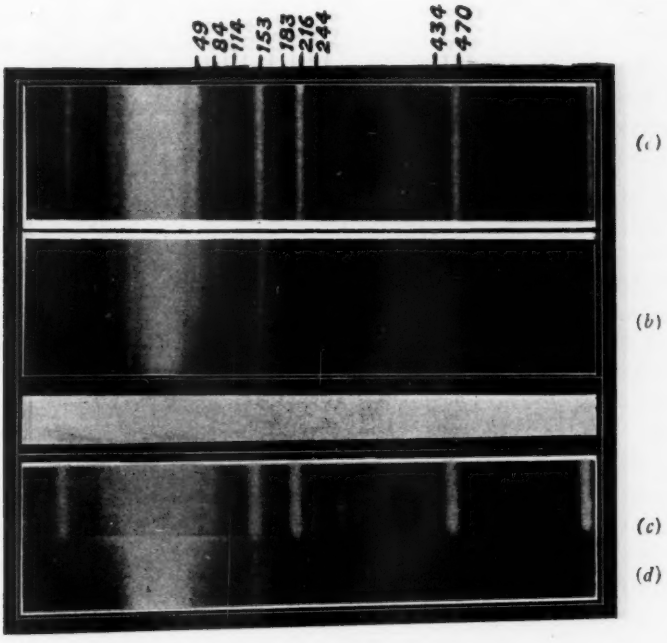


FIG. 1. Microphotograph of Raman Effect

frequency appearing as the weaker component. The second Raman line having a frequency shift of 85 is seen to cover the region from 76–90. The intense line of frequency shift 153 is seen to have an easily measurable breadth. The 216 line is sharper, but has a weaker companion barely resolved from it with a frequency shift of 211. The line with a frequency shift of 470 is also fairly sharp.



Raman Spectra of Sulphur

(*a*) & (*c*) Crystal—Two-Prism Spectrograph
(*b*) „ Littrow
(*d*) Liquid—Two-Prism

The considerable width of the lines and especially of those with relatively small frequency shifts revealed by the spectrograms is not surprising when the very complex structure of the sulphur molecule is recalled. The unit cell, according to the published X-ray studies of Warren and Burwell (1935), contains 16 S_8 molecules, and it can scarcely be supposed that the rotational oscillations of all these molecules can have identical frequencies. It is not improbable therefore that at low temperatures the low-frequency vibrations may appear clearly resolved into several discrete components.

A comparison of the Raman spectra of crystalline and liquid sulphur was also made with the Hilger two-prism instrument. In such studies, it is usual to obtain the spectra separately and measure the frequency shifts with the aid of an iron arc comparison. As the changes, if any, are bound to be small, an obviously better method of comparison is to take the two spectra side by side on the same plate with the aid of a Hartmann diaphragm. Such a study was made for solid and liquid sulphur and no change of frequency in the two cases could be definitely established. It would be seen in the spectra reproduced as Fig. 2 in Plate XII that the low frequency lines appearing in the crystal have been replaced by a wing in the liquid. The latter terminates at about 81 $cm.^{-1}$ and there is more than a suspicion of the persistence of this line at 81 in the spectrum of the liquid. The absence of any observable differences of frequency of the internal vibrations in the liquid and solid states of sulphur indicates that the inter-molecular forces scarcely influence the internal vibrations of the sulphur molecule. The assumption made in the earlier paper that the S_8 molecules in the crystal can be considered to vibrate independently of each other is therefore justified.

In conclusion, the author's thanks are due to Sir C. V. Raman for his valuable assistance during the course of this investigation.

4. Summary

The paper briefly reports the study of the Raman spectrum of rhombic sulphur carried out with a large and clear natural crystal, made with two different spectrographs. The instrument of higher resolving power showed that the Raman lines with small frequency shifts had a noticeable breadth, suggesting that they consist of several unresolved components, while on the other hand the lines with larger frequency shifts are much sharper. These facts are not surprising in view of the complexity of the structure of the sulphur crystal, each unit cell containing 16 S_8 molecules. The frequency shifts and line breadths have been measured and recorded.

REFERENCES

1. Norris, R. .. *Proc. Ind. Acad. Sci.*, 1941, **13**, 291.
2. Warren and Burwell .. *Jour. Chem. Phys.*, 1935, **3**, 6.

THE SCATTERING OF LIGHT BY LIQUID SURFACES

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Received September 11, 1942

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1. Introduction

As early as 1908, Smoluchowski suggested that the surface of a liquid in the vicinity of the critical temperature may exhibit an optically detectable rugosity or diffusion of light in addition to the familiar phenomenon of critical opalescence exhibited by the body of the liquid. This suggestion was followed up in 1913 by Mandelstamm who developed the idea theoretically and also made some observations on the diffusion of light by the boundary between the two phases of a binary liquid mixture (CS_2—CH_4OH) near the critical solution temperature. The scope of the subject was however vastly extended when it was shown by Raman (1923) that surface scattering is a universally observable phenomenon exhibited by all liquids and at all temperatures, and is not confined to the vicinity of the critical conditions. Following this discovery, Raman and Ramdas published a series of papers (1925) describing quantitative studies of the intensity and polarisation characters of the surface opalescence of several liquids, including mercury. On the theoretical side, Gans followed up Mandelstamm and derived expressions for the intensity of scattering, the fundamental basis of his theory being that the surface agitation could be analysed into sets of trains of surface waves which diffract light in the manner of a two-dimensional grating. Somewhat later, Andronow and Leontowicz (1926), and Ramdas (1926) discussed the experimental results of Raman and Ramdas in relation to the Mandelstamm–Gans theory. However, the determinations by Ramdas of the intensity of scattering were visual and subjective and hence not altogether so trustworthy as one would wish. In the present paper, a quantitative study is made of the intensity of the surface opalescence in methyl alcohol in various azimuths and different angles of observation by the method of photographic photometry and the results are compared with theory.

2. *Experimental Arrangements and Results*

Kahlbaum's pure methyl alcohol was taken in a double bulb and further purification was carried out by the familiar method of distillation *in vacuo*. After each distillation, the liquid in the bulb was tested in a strong beam of sunlight for any speck of dust. Care was taken to see that the last distillation was made very slowly. After the final distillation the bulb was sealed off. A portion of the bulb was blackened outside so as to provide a suitable background for the observation of scattering. The experiment was carried out in a dark cabin, in the wall of which there was an aperture letting in a beam of sunlight reflected from a Foucault single mirror heliostat. A Dallmeyer lens of variable aperture and focal length 12″ was used to focus the incident illumination. Heat rays were cut off by means of alum solution contained in a cell which was placed immediately after the lens. The light was always focussed on the liquid surface.

Constant intensity of the incident radiation was secured by conducting the experiment and taking all the pictures, between 11-30 A.M. and 12-30 P.M. when the altitude of the sun and hence also the intensity of sunlight could be assumed to be almost constant. Special rapid panchromatic plates taken from the same packet were used for the photography. Exposures were given for the same time correct to a second in all positions and the development also was carried out for exactly the same interval of time for all the plates, in the same developer. A Moll microphotometer supplied by Kipp and Zonen was employed for the photographic density determination. The calibratiom of the plate was done by the method of "crossed nicols" employing sunlight itself as the source. This was necessitated by the fact that the exact wavelength of the scattered light could not be known and hence that the plate had to be calibrated for composite light. Thus the density-log intensity curve was plotted and the microphtometer readings standardized.

By the use of a yellow filter, the intensity of the surface scattering relatively to the body scattering may be increased. It is hoped on a further occasion to repeat the work using such a filter and also making the necessary correction for the body scattering which necessarily appears superimposed on the surface effect.

Case i:—The distribution of intensity in various azimuths from 0° to 90° keeping the angle of observation equal to the critical angle when the angle of incidence is nearly 40° from below has been measured experimentally for methyl alcohol and compared with the theoretical values (taken from a paper by Ramdas).

TABLE I

Azimuth in degrees measured from plane of incidence	Intensity by photographic photometry $\times 10^6$	Intensity calculated from the Gans theory $\times 10^6$	Azimuth in degrees measured from plane of incidence	Intensity by photographic photometry $\times 10^6$	Intensity calculated from the Gans theory $\times 10^6$
0°	17·8 (Assumed)	17·8	50	·27	·43
10	14·9	7·9	60	·22	·28
20	5·5	2·9	75	·15	·16
30	1·9	1·3	90	·10	·12
40	·61	·72			

Case ii :—The variation of the intensity with the angle of observation has similarly been studied from below the liquid surface. For an accurate determination of this variation a case had to be chosen in which the change of intensity due to alteration of azimuth least affects the values. This is because of the fact that the intensity variation due to azimuth change is much more marked than that due to change of angle of observation. In order to avoid this error, light was allowed to be incident normally on the liquid surface from above. In this case a change of azimush does not affect the intensity at all, and hence the variation of the latter with the angle of observation could be determined accurately.

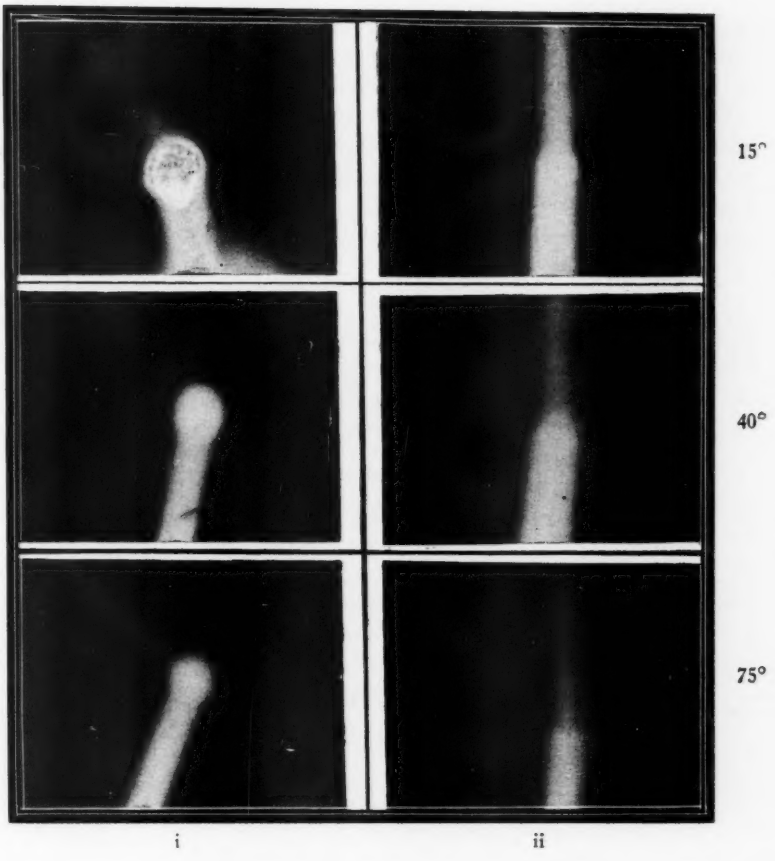
The values are tabulated below :—

TABLE II

Angle of observation	Intensity by photographic photometry	Intensity as calculated from Gans theory
90°	0 (Along the surface)	0
75°	·42	·2
60°	1·16	1·13
47° (Critical angle)	1·83 (Assumed)	1·83
40°	1·20	1·30
15°	3·10	9·50
0°	(Refracted beam)	(Refracted beam)

4. *Discussion of Results*

The figures given in Tables I and II point clearly to the fact that the discrepancies between theory and observation are greatest as regards the variation of intensity with the angle of scattering. From Table I it is seen that the theoretical and experimental values do not agree for angles 10° and



The scattering of light by methyl alcohol surface

FIG. i. Variation of intensity with azimuth of observation

FIG. ii. Variation of intensity with angle of observation

20°. This can be partially explained as due to the fact that the blackening on the plate is almost the same as far 0° and hence there are only differences of ·3 and ·2 cm. in the microphotometer reading. A slight error in this introduces a large error in the calculated intensities. The discrepancy is however, unmistakable in the variation of the intensity of scattering with the angle of scattering. True that even qualitatively there is a sudden increase of intensity as the critical angle is approached. But the abnormal jump of intensity when the refracted beam is approached which is predicted by theory is not observed in practice. This points to a fundamental inadequacy of the Gans theory which has already been indicated as probable by Raman and Jagannathan (1934).

In conclusion, the author wishes to express his gratitude to Professor Sir C. V. Raman for suggesting the problem and for the keen interest he has taken in the investigation. His thanks are also due to Mr. P. G. N. Nayar for helpful suggestions in the course of the experiment.

5. *Summary*

The variations of the intensity of the scattering of light by a liquid surface (methyl alcohol) with changes of the azimuth and of the angle of observation have been measured by the objective method of photographic photometry. The results are compared with the Mandelstamm–Gans theory and it is shown that the facts are not in accord with the theory as regards the influence of the angle of scattering, the actual change in intensity being less rapid than that indicated by the theory.

REFERENCES

1. Smoluchowski .. *Ann. d. Phys.*, 1908, **25**, 205.
2. Mandelstamm .. *Ibid.*, 1913, **41**, 609.
3. Raman .. *Nature*, 1923, **112**, 281.
4. Raman and Ramdas .. *Proc. Roy. Soc.* (A), 1925, **108**, 561 ; **109**, 150, 272.
5. Gans .. *Ann. der Phys.*, 1924, **74**, 231.
6. Ramdas .. *Ind. Jour. Phys.*, 1926, **1**, 199.
7. Andronow and Leontowicz *Zeit. f. Phys.*, 1926, **38**, 485.
8. Leontowicz .. *Ibid.*, 1928, **47**, 299.
9. Jagannathan .. *Proc. Ind. Acad. Sci.*, 1934, **1**, 115.

DERIVATIVES OF *o*-, *m*- AND *p*-AMINO-BENZAMIDES AND OTHER RELATED COMPOUNDS

By (Late) N. W. Hirwe and P. Y. Kulkarni

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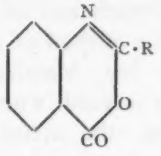
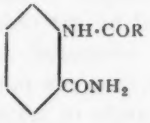
A detailed study of amides and other derivatives of *o*-, *m*- and *p*-amino benzoic acids was made as these amides were required for some other work published elsewhere in this Journal. These amides were prepared by ammoniacal hydrolysis of the acyl-anthranils and methyl esters of *m*- and *p*-amino benzoic acids.

The acylanthranils (I) are usually obtained by boiling acyl-anthranilic acid with excess of acetic anhydride and, on further treatment with ammonia (0·88 Sp.Gr.) at lower temperature they form amides (II), and at higher temperature they form the corresponding substituted quinazolones (III).



(I)



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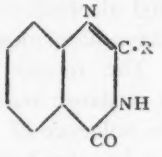

(III)

Anschutz with his co-workers[1] obtained directly 2-methyl-4-quinazolone by treating acetyl anthranil with ammonia (0·88 Sp.Gr.) at room temperature; but on similar treatment of benzoyl anthranil with ammonia even in alcoholic solution they could isolate the intermediate benzoyl-anthranilamide, which on further warming in alkaline solution was converted into 2-phenyl-4-quinazolone. They also succeeded in isolating the intermediate amide in the former case by carrying out the reaction at freezing temperature. By adopting this method the corresponding amides were isolated by the present authors from the acylanthranils, obtained from 5-bromo-2-acetylamino-benzoic acid and 5-bromo-2-benzoylaminobenzoic acid. These amides are fairly stable in cold ammoniacal solution but are converted into corresponding quinazolones on warming.

While studying the derivatives of 2-methyl-4-quinazolone various workers[2] found that the several primary amines, when heated with acetyl-anthranil at 170° give directly the correspondingly substituted quinazolones

and not the intermediate substituted amides. On similar treatment of benzoylanthranil with a few primary amines at 170° the present author obtained in all cases the intermediate substituted amides, which on heating 50° above their melting points gave the correspondingly substituted quinazolones.

Chancel[3] and Beilstein-Reichenbach[4] prepared 3-amino-benzamide and 4-amino-benzamide by the mild reduction of the corresponding nitrobenzamides and also their acetyl derivatives were indirectly prepared from the corresponding amino-nitriles.[5] The present authors prepared the required acetyl and benzoyl derivatives of these amides in improved yields from amino benzoic acids by the following method. The methyl esters of these amino benzoic acids were first prepared by HCl-esterification method, which were already prepared by Cahours[6] and Einhorn-oppenheimer[7] by other indirect methods. These esters after acylation were shaken with liquor ammonia (0·88 Sp.Gr.) to get the amides.

Experimental

5-*Bromo*-2-*acetylamino-benzamide.*—The acylanthranil, obtained from 5-bromo-2-acetyl amino-benzoic acid (10 g.) was shaken with ammonia (100 c.c.; 0·88 Sp.Gr.) for four hours and was kept in refrigerator overnight. The separated amide (7 g.) crystallised from dilute alcohol in square plates. M.P. 194°. (Found: N, 10·9, $C_9H_9N_2O_2Br$ requires N, 10·9 per cent.)

5-*Bromo*-2-*benzoylamino-benzoic acid.*—Benzoylchloride (8 g.) was slowly added to a cooled solution of 5-bromo-2-amino-benzoic acid (10 g.) in sodium hydroxide (100 c.c.; 10%), when much heat was evolved. After heating for half an hour on water-bath the mixture was cooled and neutralised. The separated solid on washing free from benzoic acid crystallised from dilute alcohol in white needles. M.P. 260°. (Found: Br, 25·2; $C_{14}H_{10}NO_3Br$ requires Br, 25·0 per cent.)

2-*Phenyl*-6-*bromo*-1 : 3-*benzoxazine*-4-*one.* (6-*Bromo-benzoyl-anthranil*). —5-Bromo-2-benzoylamino-benzoic acid (5 g.) and acetic anhydride (50 c.c.) were refluxed together for eight hours. After distilling off the excess of acetic anhydride the mixture was poured in iced water. The separated solid (3·5 g.) crystallised from dilute alcohol. M.P. 193–94°. (Found: N, 4·3; Br, 26·4; $C_{14}H_8NO_2Br$ requires N, 4·6; Br, 26·5 per cent.)

5-*Bromo*-2-*benzoylamino-benzamide.*—2-Phenyl-6-bromo-1 : 3-benzoxazine-4-one (5 g.) and ammonia (50 c.c.; 0·88 Sp.Gr.) were shaken together for four hours and kept overnight in refrigerator. The separated solid (4 g.) crystallised from alcohol in rectangular plates, m.p. 211-12°. (Found: N, 8·6; Br, 25·1; $C_{14}H_{11}N_2O_2Br$ requires N, 8·8; Br, 25·1 per cent.)

2-*Phenyl*-5-*bromo*-4-*quinazolone*. — 5-Bromo-2-benzoylamino-benzamide (2 g.) was warmed in dilute ammonia (20 c.c.) till all went in solution. On acidification with dilute acetic acid a solid (15 g.) separated which crystallised from nitrobenzene. Does not melt below 300°. (Found: C, 55·2; H, 3·2; Br, 26·3; $C_{14}H_9H_2OBr$ requires C, 55·8; H, 3·0; Br, 26·6 per cent.)

2-3-*Diphenyl*-4-*quinazolone*.—2-Benzoylamino-benzanilide (2 g.) was heated in a tube immersed in sulphuric acid bath at about 300° for half an hour till all the moisture had escaped from the melted liquid. On cooling the melt was extracted with alcohol and refluxed with animal charcoal for six hours. The product (1 g.) crystallised from dilute-alcohol in small granules, m.p. 186°. (Found: C, 80·7; H, 4·6; $C_{20}H_{14}N_2O$ requires C, 80·5; H, 4·7 per cent.)

2-*Benzoyl-amino-benz*-m-*toluidide*.—Benzoylanthranil (5 g.) and *m*-toluidine (5 g.) were heated together at 170° in a tube for two hours. The reaction mixture was allowed to stand overnight. The melt was freed from *m*-toluidine by dilute hydrochloric acid and the product (5·6 g.) after refluxing with animal charcoal in alcohol was crystallised from dilute alcohol, m.p. 220° C. (Found: C, 76·7; H, 5·3; $C_{21}H_{18}N_2O_2$ requires C, 76·4; H, 5·5 per cent.)

2-*Phenyl*-3-m-*tolyl*-4-*quinazolone*.—2-Benzoylamino-benz-*m*-toluidide (2 g.) was heated in a tube immersed in sulphuric acid bath at 250° for half an hour. The melt after refluxing with animal charcoal in alcohol crystallised from dilute alcohol in small granules, m.p. 145°. (Found: C, 80·9; H, 5·6; $C_{21}H_{16}N_2O$ requires C, 80·8; H, 5.1 per cent.)

2-*Benzoyl-amino-benzoyl-hydrazine*.—Benzoylanthranil (5 g.) and hydrazine hydrate (10 c.c.) were shaken together for 48 hours and poured into water when a yellowish mass separated out. The product (5·0 g.) crystallised from dilute alcohol in yellowish long needles, m.p. 176°. (Found: C, 66·0; H, 5·3; $C_{14}H_{13}N_3O_2$ requires C, 65·9; H, 5·1 per cent.)

2-*Phenyl*-3-*amino*-4-*quinazolone*.—2-Benzoylamino-benzoyl-hydrazine (2 g.) was heated in a tube immersed in sulphuric acid bath at 220° for half an hour. The melt on cooling was extracted with alcohol and crystallised from dilute alcohol in needles, m.p. 184–86°. (Found: C, 71·2; H, 4·9; $C_{14}H_{11}N_3O$ requires C, 70·9; H, 4·9. per cent.)

3-*Acetyl amino-benzamide*, 3-*Benzoylamino-benzamide*, 4-*Acetyl-amino-benzamide and* 4-*Benzoylamino-benzamide*.—These amides were prepared by

the following method :—A solution of amino-benzoic acid (20 g.) dissolved in methyl-alcohol (400 c.c.) was saturated with dry hydrochloric acid below 10°. The solution was kept overnight and then refluxed for 18 hours without contact of moisture. The excess of methyl alcohol was distilled off, the residue was made alkaline by sodium carbonate when the methyl ester of the amino-acid separated as an upper layer. It was extracted with ether and after drying over calcium chloride, was acetylated and benzoylated according to usual methods. The resulting esters (5 g.) of acylamino benzoic acids were shaken with an excess of ammonia (100 c.c.; 0·88 Sp.Gr.) for eight hours. The excess of ammonia was evaporated and resulting amide was crystallised from alcohol. Methyl-*p*-benzoyl-amino-benzoate was required to be heated under pressure at 70° C. in methyl alcohol saturated with ammonia to get the amide.

3-*Benzoylamino-benzamide.*—m.p. 233°. (Found: N, 11·6; $C_{14}H_{12}N_2O_2$ requires N, 11·7 per cent.)

Methyl-4-*acetylamino-benzoate.*—m.p. 114°. (Found: C, 62·3: H, 6·1; $C_{10}H_{11}NO_3$ requires C, 62·2; H, 5·7 per cent.)

Methyl-4-*benzoylamino-benzoate.*—m.p. 160°. (Found: C, 70·3; H, 5·3; $C_{15}H_{13}NO_3$ requires C, 70·6; H, 5·1 per cent.)

4-*Benzoylamino-benzamide.*—m.p. 284–85°. (Found: N, 11·3; $C_{14}H_{12}N_2O_2$ requires N, 11·7 per cent.)

REFERENCES

1. Anschutz Schmidt and Greiffenberg .. *Ber.*, **35**, 3481.
2. Bogert and Beal .. *J.A.C.S.*, **34**, 518.
   Bogert Gortner .. *Ibid.*, **33**, 949.
   Anschutz Schmidt and Greiffenberg .. *Loc. cit.*
3. Chancel .. *C. R.*, **28**, 293 ; *Annal*, **72**, 276.
4. Beilstein Reichenberg .. *Annalen*, **132**, 144.
5. Bogert and Beans .. *J.A.C.S.*, **26**, 476 ;
   Bogert Wise .. *Ibid.*, **32**, 1496.
6. Cahours .. *A. Ch.*, (3), **53**, 331 ; *Annalen*, **109**, 16.
7. Sudburrough and Beard .. *J.C.S.*, **97**, 786.

HYSTERESIS IN SORPTION VII

Scanning of the Hysteresis Loop. Alumina Gel-Water System

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(Communicated by Prof. B. Sanjiva Rao, M.A., Ph.D., F.A.Sc.)

Introduction

The permanence and reproducibility of the hysteresis effect in sorption has been established in various systems such as, titania gel-water,[1,3] silica-gel-water,[4] alumina gel-water,[2] silica gel-carbon tetrachloride,[5] ferric oxide gel-carbon tetrachloride.[6] A permanent and reproducible hysteresis loop can be traversed from various points on the sorption and desorption curves. Such a study called the scanning of the hysteresis loop has been made in several systems (*loc. cit.*). The study of the scanning of the permanent and reproducible hysteresis loop in alumina gel-water system[8] has been presented in this paper.

Experimental

Alumina gel employed in this work was prepared according to the method described in an earlier paper[7] and is a sample of the activated gel used in the previous study on the permanence of the hysteresis loop in sorption.[2] The gel was activated by heating it to 950° C. for 2 hours. The activated gel was degassed in vacuum (10^{-2} mm.) for 6 hours.

The quartz fibre spring technique, described in Part I[3] was employed in the present work. A series of sorptions and desorptions of water vapour on alumina gel at 30° C. was effected. Sorption was effected by introducing air-free water vapour into the sorption tube and desorption by removing water vapour by means of a Cenco-Hyvac pump. In sorption and desorption sufficient time was always allowed for the attainment of equilibrium.

Scanning of the Hysteresis Loop

The permanent hysteresis loop in alumina gel-water system, which is reproduced ten times, has been indicated in a former communication.[2] For scanning of the loop, a reproducible loop had again to be obtained as a separate sample of the same activated gel was employed in the present study. Four cycles of sorptions and desorptions were conducted. The third and fourth hysteresis loops are identical (Fig. 1). The fourth loop was scanned.

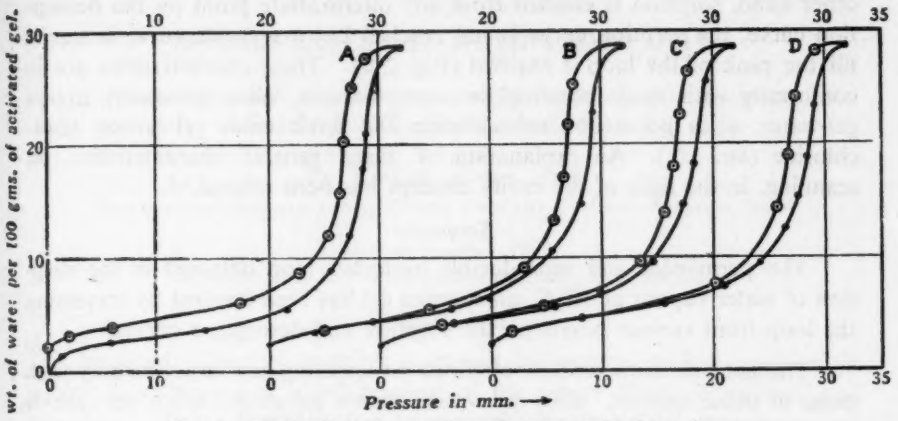

FIG. 1. Hysteresis in the sorption of water on alumina gel
A—First sorption • and desorption ⊙
B—Second „ „ „
C—Third „ „ „
D—Fourth „ „ „

The sorptive capacity of the gel at saturation pressure is 28·52 gm. of water per 100 gm. of activated gel. Time required for completing four cycles of sorption and desorption is over 2 months and time for completing scanning is 10 days. Water irreversibly held by the activated gel at the end of first desorption is 2·25 gm. per 100 gm.

The hysteresis loop has been scanned by traversing it from various intermediate points on the sorption and desorption curves. If desorption is effected from any intermediate point on the sorption curve, the hysteresis loop is crossed and the desorption curve is reached (Fig. 2 A). If, on the

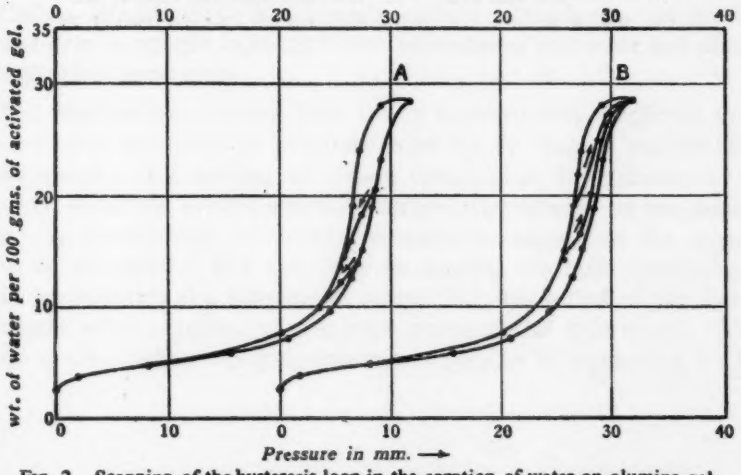

FIG. 2. Scanning of the hysteresis loop in the sorption of water on alumina gel

in water in a vacuum flask. The slow and continuous evaporation of water in the vacuum flask would always keep its temperature slightly below that of the thermostat.

Permanence of the Hysteresis Loop

A series of sorptions and desorptions of carbon tetrachloride at 30°C. on titania gel was conducted. Sorption was effected by exposing the degassed activated gel to air-free carbon tetrachloride vapour and desorption by the removal of the vapour by a Cenco Hyvac pump. Complete equilibrium was allowed to attain before taking a measurement. The first, second, third and twelfth hysteresis loops have been indicated in Fig. 1. After the

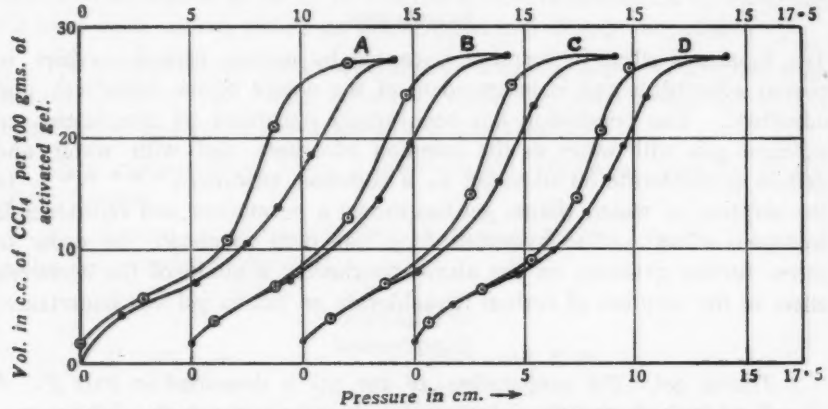

FIG. 1. Hysteresis loop in the sorption of carbon tetrachloride on titania gel
A—First sorption · and desorption ⊙
B—Second „ „ „
C—Third „ „ „
D—Twelfth „ „ „

first cycle of sorption and desorption the hysteresis loop remains permanent and reproducible, the second loop being identical with subsequent loops. The time required for completing the twelfth cycle is nearly a month. The sorptive capacity of the gel for carbon tetrachloride at saturation pressure is 27·32 gms. per 100 gms. of the activated gel.

Just like silica[5,6] titania gel shows the hysteresis effect with water as well as carbon tetrachloride. The sorptive capacity for carbon tetrachloride is practically the same as that for water. The general shape and size of the loop with carbon tetrachloride are almost the same as those with water. All these facts are interpretable on the basis of the cavity concept.

In any porous adsorbent, the total capillary volume determines the total sorptive capacity. The cavities cause the hysteresis effect. The

mechanism of filling and emptying of cavities and the entrapping of excess liquid by the cavities during desorption causing the hysteresis effect, have been discussed elsewhere[2]. The area of the hysteresis loop is probably a measure of the total cavity volume. The general shape of the hysteresis loop is connected with the shape of the cavities. In any rigid porous adsorbent, the total capillary volume, the cavity volume and the shape of the cavities remain the same irrespective of the nature of adsorbate used in sorption. It follows from the cavity concept that sorption and desorption should always produce hysteresis effect with all adsorbates and that the hysteresis loops with all adsorbates must practically be the same in size and shape. The nature of the adsorbent and adsorbate is of no importance in hysteresis in sorption. The shape and size of the hysteresis loop are dependent upon the shape and size of the cavities in the porous adsorbent.

Scanning of the Hysteresis Loop

A permanent and reproducible hysteresis loop can always be scanned by traversing the loop from various points on the sorption and desorption curves. Such scanning has been effected of the hysteresis loop in titania gel-carbon tetrachloride system[9]. The general characteristics of the results obtained on scanning are the same as those of other systems, silica gel-water[5], titania gel-water[4], alumina gel-water[8], silica gel-carbon tetrachloride[6], ferric oxide gel-carbon tetrachloride.[7]

If at any point on the sorption curve, desorption is effected, the loop is crossed and the desorption curve is reached (Fig. 2A). If sorption is effected from any point on the desorption curve, separate curve is traced till the peak of the loop is reached (Fig. 2B). An interpretation of such

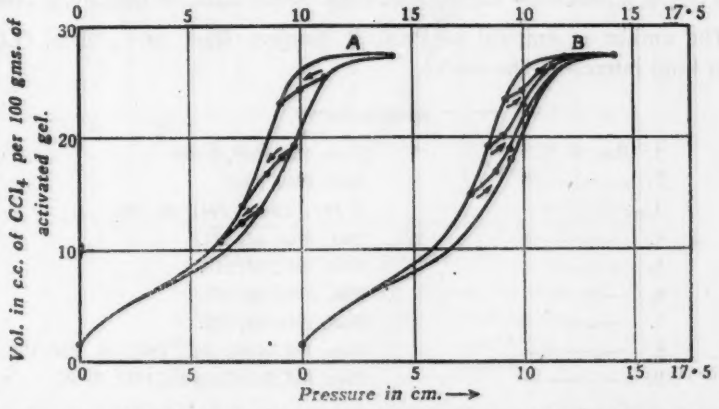

FIG. 2. Scanning of the hysteresis loop in the sorption of carbon tetrachloride on titania gel

results on scanning, in the light of the cavity concept has already been offered[1, 4]. The cavity concept predicts the other possibilities of reaching the sorption curve from any point on the desorption curve and of reaching the tail-end of the loop from any point of the sorption curve. Such possibilities have not been observed so far in the systems investigated.

The new method of study—the scanning—of the permanent and reproducible hysteresis loop in titania gel-carbon tetrachloride system just as in various other systems (*loc. cit.*) has yielded results having certain general characteristics which form a strong evidence in support of the cavity concept. No other theory of the hysteresis effect in sorption, advanced so far, can explain these interesting characteristics.

Summary

In a series of sorptions and desorptions of carbon tetrachloride at 30°C. on titania gel, a permanent hysteresis effect is obtained. The hysteresis loop has been reproduced in the twelfth cycle of sorption and desorption.

The reproducible hysteresis loop has been scanned. The general characteristics of the results on scanning are in conformity with those of other systems, titania gel-water, silica gel-water, alumina gel-water, silica gel-carbon tetrachloride, ferric oxide gel-carbon tetrachloride.

The hysteresis effect in sorption is caused by cavities in the porous adsorbent. The shape and size of the hysteresis loop are dependent upon the shape and size of the cavities and are independent of the nature of the adsorbate. The general characteristics of the results on scanning of the hysteresis loop are independent of the nature of the adsorbent and adsorbate. These characteristics are explainable only on the basis of the cavity concept.

The author is grateful to Prof. B. Sanjiva Rao, M.A., PH.D. (Lond.), for his kind interest in the work.

REFERENCES

1. Rao, K. S. .. *Curr. Sci.*, 1939, **8**, 468.
2. ———— .. *Ibid.*, 1940, **9**, 68.
3. ———— .. *J. Phys. Chem.*, 1941, **45**, 500.
4. ———— .. *Ibid.*, 1941, **45**, 507.
5. ———— .. *Ibid.*, 1941, **45**, 513.
6. ———— .. *Ibid.*, 1941, **45**, 517.
7. ———— .. *Ibid.*, 1941, **45**, 522.
8. ———— .. *Proc. Ind. Acad. Sci.*, 1942, **16**, Part VII.
9. ———— .. *Proc. Ind. Sci. Congress*, 1942, **3**, 66.

HYSTERESIS IN SORPTION IX

Effect of Temperature on the Hysteresis Loop. Silica Gel-Water System

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Introduction

SOME years ago, the problem of hysteresis in sorption was obscure and the very reality of the effect uncertain. The recent investigations on a large number of variety of systems have proved beyond doubt, the reality and the reproducibility of the effect.[1] The effect of varying temperatures on such a permanent and reproducible hysteresis loop[4] has been the object of the study presented in this paper. Silica gel-water system was chosen for this study.

Experimental

The technique employed is the McBain-Bakr quartz fibre spring technique.[2] After the study of the permanence and scanning of the hysteresis loop with silica gel[3] was completed, the present studies of the hysteresis effect at varying temperatures were continued on the same sample of the gel. Sorption and desorption were effected at 30° C. 35° C., and 40° C. The hysteresis loops have been indicated in Fig. 1.

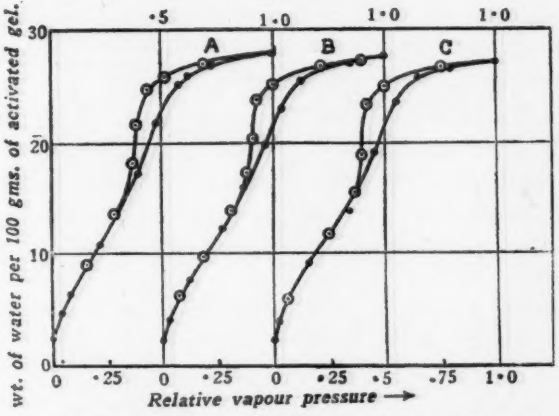

FIG. 1. Hysteresis in the sorption of water on silica gel
A—Sorption · and desorption ⊙ at 30° C.
B— „ „ „ „ at 35° C.
C— „ „ „ „ at 40° C.

The air thermostat of the type constructed by Vernon[5], with the modifications described in Part I[2] was suitably adjusted to temperatures of 35° C. and 40° C. while studying hysteresis at these temperatures. To maintain these temperatures, the temporary heaters had to be permanently switched on and the controlled heaters had to be replaced by more powerful ones.

Discussion

To facilitate a comparative study of the hysteresis loops at different temperatures, the sorptive capacities of the gel are plotted against the relative vapour pressures instead of the actual pressures (Fig. 1). The sorptive capacities of the gel for water at 30° C., 35° C. and 40° C. are 27·71 gm., 27·36 gm. and 27·01 gm. respectively per 100 gm. of activated gel. The figure shows that at the three different temperatures, the hysteresis effect remains permanent. The three loops are practically identical with regard to their shape and size. There is however a slight decrease in the sorptive capacities at saturation pressure with increase of temperature. An identity of the hysteresis loops is to be expected in the light of the cavity concept. In all porous adsorbents major part of sorption is due to condensation of the vapour of the liquid in the capillaries. If the adsorbent is rigid, the total capillary volume remains unaltered irrespective of the temperature at which sorption is conducted. Of the total capillary volume, the cavity volume remains the same and therefore the hysteresis loop caused by cavities will be the same at different temperatures. The shape and size of the cavities of the porous adsorbent remaining unaffected at different temperatures, the shape and size of the hysteresis loops should be the same and this has been borne out by facts presented in this paper.

Summary

Sorption and desorption of water vapour at 30° C., 35° C. and 40° C. on silica gel have been conducted. The hysteresis effect is exhibited at all these three temperatures and the hysteresis loops are all identical.

Such an identity of the hysteresis loops, at different temperatures, in any rigid porous adsorbent is satisfactorily explainable in the light of the cavity concept.

The author is grateful to Prof. B. Sanjiva Rao, M.A., PH.D. (Lond.), for his keen interest in the work.

REFERENCES

1. Rao, K. S. .. *J. Phys. Chem.*, 1941, **45**, 500–39.
2. ———— .. *Ibid.*, 1941, **45**, 500.
3. ———— .. *Ibid.*, 1941, **45**, 513.
4. ———— .. *Proc. Ind. Sci. Congress*, 1942, **3**, 67.
5. Vernon .. *Trans. Faraday Soc.*, 1931, **27**, 241.

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